

Chemometric Study of Graft Copolymerization of Guar-g-(acrylamide-co-diallyl dimethylammonium chloride)

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ABSTRACT: Chemometrics was employed to study the effect of various reaction conditions on the graft copolymerization of acrylamide (AM) and diallyl dimethylammonium chloride (DADMAC) onto guar gum using the cerous sulfate and potassium persulfate complex initiation system. A two level full factorial design was used to study the effect of reaction parameters on percentage grafting (%G) and monomer conversion (%MC). Synthesized polymers were characterized using Fourier transform infrared spectroscopy (FTIR), ¹H-NMR (nuclear magnetic resonance spectroscopy), and ¹³C-NMR and also were analyzed for differences in intrinsic viscosity and charge incurred with changing reaction conditions. The concentration of AM was observed to have the greater effect on %grafting. Interaction effects between the reaction temperature and concentration of AM were also found to be important. Under the reaction condition studied, the highest grafting (%G) was obtained for polymer 1 (0.7M AM concentration, 60°C reaction temperature, and 1M acid concentration). © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: guar gum; graft copolymers; chemometrics, main effects and interactions effects; radical polymerization; NMR

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INTRODUCTION

Guar gum is a D-galactopyranose-D-mannoglycan (1 : 2), consisting of a principal backbone chain of (1-4)-β-D-mannopyranosyl units, with single (1-6) α-D-galactopyranosyl units as side branches.^{1,2} Guar gum is used in numerous industrial applications such as cosmetics, textile, pharmaceuticals, and the pulp and paper industry, to name a few. It is mainly used as filler, a viscosity builder, and a water binder.³ Although an advantage, the viscosity is difficult to control because of the biodegradability of guar gum. Its susceptibility to bacterial attack can be overcome by preparing graft copolymers of guar gum.⁴ Modification of guar gum by grafting results in the retention of the desirable properties and at the same time gives the opportunity to incorporate other properties⁴ by the addition of both charged and neutral monomers. Grafted guar gum is used in the preparation of flocculants for industrial applications and as a biodegradable drag reducing agent.^{5,6}

Intensive work has been carried out over the past few decades on graft polymerization and its applications. A variety of monomers have been grafted on different natural polymeric systems

such as polyacrylonitrile on wood fibres,^{7,8} acrylamide (AM) onto hydroxypropyl guar gum,⁹ styrene, and acrylonitrile onto starch.¹⁰ AM has been found to be a useful monomer for grafting onto different types of polysaccharides such as starch, cellulose,¹¹ and guar gum.⁵ AM's effectiveness in terms of flocculation, solubility, thermal stability, binding strength, water retention, and drag reducing effectiveness has been found to increase on grafting.⁵

McLean et al. reported the synthesis of a graft copolymer of AM and diallyl dimethylammonium chloride (DADMAC) onto guar gum, which showed very promising results for the application in the pulp and paper industry to control problematic deposition of wood resins.¹² No attempts were made in that work to optimize the polymerization reaction.

This article presents the results of the effect of three major reaction parameters on the graft copolymerization of guar-g-(AM-co-DAMAC) and also physical properties of the synthesized polymers produced under varying reaction conditions. Experiments were designed using a chemometric approach so that individual main effects and interaction effects between the

reaction parameters could be studied. This approach has benefits over the more traditional systematic approach of varying one parameter at a time while keeping the others constant¹³:

1. Fewer experiments are required saving both cost and time required for the experiments.
2. Synergetic effects of two or more factors can be quantified.

These effects are very difficult to establish one at a time.

The traditional systematic approach, as stated by Palasota and Deming¹⁴ often results in an incomplete understanding of the behavior of the system and lack of predictive ability. This study aims to set up the platform for further modeling and optimization of the reaction conditions. The AM concentration, reaction temperature, and acid concentration were chosen from the range of reaction conditions for this study as they were identified from the literature as being key parameters in the graft polymerization reaction.^{15–18}

EXPERIMENTAL

Purification of Guar Gum

Purification of guar (Fluka, CAS: 9000-30-0) was carried out using the process reported by Rayment et al.¹⁹ In brief, approximately 10 g of guar gum was boiled with 40 mL of 70% ethanol for 1 h under reflux. The sample was filtered, washed with 95% ethanol, and oven dried before use.

Graft Copolymerization of Guar Gum

Purified guar gum (1 g) was dissolved in water (250 mL), stirred and heated to desired temperature (60°C) under constant purging of N₂. A known amount of copper sulphate (0.1M, 10 mL) and sulfuric acid (1M, 40 mL) were added to the reaction mixture. To this solution, a known concentration of cerous (III) sulfate (3 mM, 20 mL) and potassium persulfate (5 × 10⁻² M, 20 mL) were added, followed by DADMAC (0.3M, 90 mL)²⁰ and a known amount of AM (0.7M, 110 mL).²⁰ The mixture was stirred for 2 h and quenched with hydroquinone solution (0.54M, 5 mL). The polymer was precipitated in excess amount of cold acetone (Merck, AR grade). The whole solution was then dialyzed using cellulose membrane tubing (Sigma D-9402, 76 mm, >12,000) and freeze dried to obtain the crude product.

The crude product was Soxhlet extracted with 1 : 1 mixture of glacial acetic acid and acetone for 3 h. This product was then washed with 95% ethanol (AR grade) and dried in vacuum oven and stored in desiccators before any further analysis. The resulting product was the final pure product. All the polymers synthesized were characterized using FTIR, ¹H-NMR, and ¹³C-NMR.

All the characteristic spectroscopic peaks of the purified polymer are listed as follows:

Polymer 1. ¹H-NMR 400 MHz (D₂O) δ ppm: 7.00 (–NH, AM), 3.52–4.40 (*m*, guar), 3.13–3.40 (DADMAC, CH₂), 3.02 (DADMAC, N–CH₃), 2.20–2.50 (AM, –CH)

¹³C-NMR 400 MHz (D₂O) δ ppm: 182.2 (AM, –C=O), 99.8–105.1 (guar), 70.5–81.5 (guar), 71.1 (DADMAC, CH₂), 67.3–70.2 (guar), 52.0–55.5 (DADMAC, N–CH₃)

FTIR: 3343 cm⁻¹ (guar–OH), 3195 cm⁻¹ (AM–NH), 2931 cm⁻¹ (guar–CH), 1655 cm⁻¹ (AM–CO), 1611 cm⁻¹ (AM–NH

bending), 1450, 1416 cm⁻¹ (monomers–CN stretching), 1149, 1058, 1020 cm⁻¹ (guar–COC stretching).

All the other polymers were synthesized as per the experimental design and the coded values reported in Table I, varying only the concentration of AM, reaction temperature, and acid concentration, in that sequence. Each synthesized polymer was characterized using FTIR, ¹H-NMR, and ¹³C-NMR (data not presented).

Fourier Transform Infrared Spectroscopy

The dried fixative samples were mounted on a diamond crystal and characterized by Fourier transform infrared spectroscopy (FTIR) using a Perkin Elmer Spectrum 100 FTIR Spectrometer (4000–650 cm⁻¹ wavelength, 16 scans, 8 cm⁻¹ resolution with standard mid infrared detector).

Nuclear Magnetic Resonance Spectroscopy

Data were acquired on a Varian Inova spectrometer with an Oxford 9.4 Tesla magnet with proton and carbon resonance nominally at 400 and 100 MHz, respectively. Three probes were used: 5-mm PFG probe with Z-axis gradient, 5/10 mm broadband probe and a 45 μL sample ¹³C-optimized nanoprobe with magic angle spinning at 1750 Hz. Samples with sufficient solubility were run in the first two probes and slurries of less soluble material were run in the last.

Proton 1D spectra were obtained typically with 16–32 K data-points, 128 transients, a 45-degree excitation pulse, a 1 s relaxation delay, and spectral width appropriate to the chemical shift range of individual samples. A standard, Varian 1D pulse and acquire sequence was employed in ¹³C decoupled and NOE mode. Data were processed with zero filling to twice the number of acquired data points, and exponential multiplication with a line broadening value of 0.5–1 Hz. Carbon 1D spectra were recorded in a similar manner to above in ¹H decoupled and

Table I. Two Level Factorial Experimental Design Showing All Three Reaction Parameters and Their Respective Coded Values in Parentheses 1

Polymer	Acrylamide concentration (AM) (M)	Reaction temperature (°C)	Acid concentration (M)
1	0.7 (+)	60 (+)	1.0 (+)
2	0.15 (–)	60 (+)	1.0 (+)
3	0.7 (+)	30 (–)	1.0 (+)
4	0.15 (–)	30 (–)	1.0 (+)
5	0.7 (+)	30 (–)	0.5 (–)
6	0.15 (–)	30 (–)	0.5 (–)
7	0.7 (+)	60 (+)	0.5 (–)
8	0.15 (–)	60 (+)	0.5 (–)
9	0.3	60 (+)	1.0 (+)
10	0.7 (+)	45	1.0 (+)
11	0.7 (+)	60 (+)	3.0

They are extra experiments performed at the centre points of the coded respective values of three parameters studied.

^aPolymer 9, 10, and 11 are not the part of the experimental design and were synthesized at intermediate points to understand the behavior of the three reaction parameters.

NOE mode with 64 K data points, upward of 3000 transients, a 2 s relaxation delay, and a chemical shift range of 220 ppm. Data were processed with zero filling to twice the number of acquired data points and an exponential multiplication applied with line broadening of 2–5 Hz depending on the sample.

2D COSY spectra were acquired with $2K \times 128$ data points and 64–128 transients with spectral width ascertained from 1D experiments. Ninety-degree shifted sine-bell window functions were applied in data processing and data were twice zero filled in the direct dimension and zero filled and linear predicted in the indirect dimension to a final size of $4K \times 1K$ data points. In $^1\text{H-NMR}$, a broad D_2O peak was observed at $\sim 4.56\text{--}5.02$ ppm. $^{13}\text{C-NMR}$ spectra were referenced against TMS (tetramethyl silane).

Evaluation Parameters

The level of grafting was determined by the % grafting²⁰

$$\% \text{ Grafting} = \frac{\text{Weight of (pure product - guar gum)}}{\text{Weight of guar gum}} \times 100\% \quad (1)$$

The efficiency of grafting was calculated in two ways: one based on the total amount of monomers added (%GE1) and the other based on the amount of reacted monomers (%GE2).

$$\% \text{ Grafting efficiency } 1 = \frac{\text{Weight of (pure product - guar gum)}}{\text{Weight of total monomer}} \times 100\% \quad (2)$$

$$\% \text{ Grafting efficiency } 2 = \frac{\text{Weight of (pure product - guar gum)}}{\text{Weight of reacted monomer}} \times 100\% \quad (3)$$

The amount of reacted monomer that was grafted was determined by the % monomer conversion (%MC) [eq. (4)] and the amount of monomer that formed homopolymer was also determined [eq. (5)].

$$\% \text{ MC} = \frac{\text{weight of grafted chains} + \text{weight of homopolymers}}{\text{weight of guar gum}} \times 100\% \quad (4)$$

% Homopolymer

$$= \frac{\text{Weight of impure products} - \text{weight of pure product}}{\text{Weight of impure product}} \times 100\% \quad (5)$$

Chemometrics

A two-level full factorial design incorporating additional points to obtain extra information was employed in this study. The two-level full factorial design requires $2^3 = 8$ experiments in which three variables (AM concentration, reaction temperature, and acid concentration) are considered at two different levels [high (+) and low (-)].

Table I shows the design matrix for the experiments and the reaction conditions investigated. The design matrix is a list of the eight possible coded combinations, using (+) and (-), for the factorial experimental design in which each of the eight possible combinations appears exactly once.²¹ Three additional points (polymers 9, 10, and 11), not part of the factorial design, were performed at the centre points of the coded values of the variables studied. The design shown is the same as that developed by Yates.¹

Linear statistical analysis was employed using Microsoft Excel. An average of all the high (+) and all the low (-) coded values for each of the analysis parameters was obtained. The main effects of the individual variables (AM, acid, and temperature) were determined from the difference between the high and low averages. In the same way, all possible interactions of factors were estimated.²¹

The difference between the high and low coded values was determined as a slope that was then normalized and used to detect any outliers. Outliers were considered to be anything outside the 95% confidence interval or two standard deviations from the mean. A one factor ANOVA at $P < 0.5$ was carried out on various types of effects using Microsoft Excel.

Viscosity Measurements

Viscosity measurements were undertaken on 1% w/o fixative solutions using Ubbelohde viscometer at $(18 \pm 0.1)^\circ\text{C}$. Measurement of the times for fixative solutions of various concentrations in relation to the time for water to pass the top and bottom timing lines were used to calculate the intrinsic viscosity $[\eta]$ of each fixative.²² Each measurement was carried out in triplicate and averaged.

Charge Density Measurements

The charge density was determined on 1% fixative solution of the polymers by titrating an aliquot against an anionic titrant with known charge. The Mütek PCD-02 Particle Charge Detector was utilized, with 0.001N polyethene sodium sulfonate (PES-Na, Mütek Analytic) as the anionic titrant. The PES-Na was added in small increments, with constant mixing, until charge neutralization was obtained. Based on the volume of PES-Na required to neutralize the polymer, the polymer charge was determined. For anionic polymers 0.001N poly(DADMAC) [p(DADMAC)] was used as a cationic titrant. The charge on the polymer was calculated from the volume of the titrant consumed using eq. (6) reported by Radosta et al.²³

$$Q_m = \frac{V_{\text{PES-Na}} \times C_{\text{PES-Na}}}{V_{\text{copolymer solution}} \times C_{\text{copolymer solution}}} [\text{g}^{-1}] \quad (6)$$

where $V_{\text{PES-Na}}$ is the volume of the anionic PES-Na solution in L, $C_{\text{PES-Na}}$ the molar concentration of the PES-Na solution in mol/L, $V_{\text{copolymer solution}}$ the volume of the copolymer solution titrated (fraction) in mL, and $C_{\text{copolymer solution}}$ the concentration of the copolymer solution titrated (fraction) in g/mL. Q_m is the average mass-specific charge.

RESULT AND DISCUSSION

Characterization

FTIR. Confirmation of grafting for all the polymers synthesized was conducted using FTIR. Figure 1 compares the spectra of

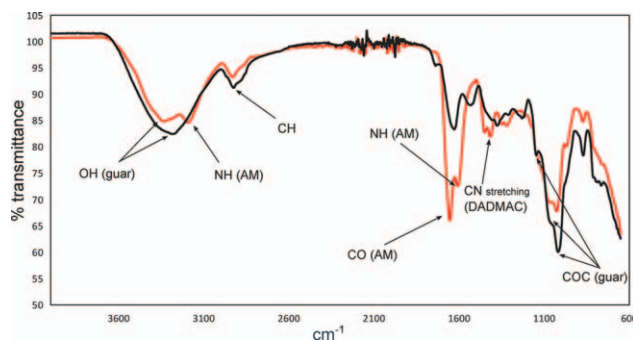


Figure 1. FTIR spectra of purified guar gum (dark/ black line) and guar-g-p(AM-co-DADMAC) grafted copolymer (light/ gray line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

purified guar and the grafted copolymer 1. A broad peak at 3343 cm^{-1} indicates the presence of (OH) stretching vibrations of the guar gum backbone.^{24,25} The protuberance at 3195 cm^{-1} shows the presence of N–H stretching vibrations from the AM unit of the copolymer.^{4,26} This extra contribution over the OH stretching frequency confirms the presence of AM in the grafted copolymer. Sharp peaks at 1655 and 1611 cm^{-1} are assigned to CO (carbonyl) stretching and NH bending vibrations of AM, respectively.^{27,28} Peaks at 1450 and 1416 cm^{-1} are known to be from CN stretching vibrations, showing the presence of both AM and DADMAC.^{29,30} The guar gum spectrum was found to have none of these assigned peaks. Peaks at 1149 , 1058 , and 1020 cm^{-1} confirmed the presence of the guar backbone as these peaks are assigned to C–O–C stretching vibrations of the polysaccharide backbone.

¹H-NMR. Figure 2 shows the ¹H NMR spectra of the grafted copolymer. To achieve complete structure elucidation comparative studies were conducted in which AM and DADMAC were individually grafted onto the guar gum backbone (data not shown). A multiplet at δ 1.67–1.78 ppm has been assigned to (*H_f*) methylene protons while the multiplet at δ 2.20–2.50 ppm is allocated to methine protons (*H_g*) of AM. Confirmation of these assignments was drawn from the similar trend and values reported by Liu et al.,³¹ Vu and Cabestany,³² and other authors.^{3,33,34}

An interesting feature of the spectra in Figure 2 was the emergence of peaks at δ 7.00 and 7.52–7.99 ppm, which can be assigned to the amide protons (*H_h*). Ideally, these protons should be exchanged with deuterium from heavy water, however, the presence of these peaks indicate that exchange of amide protons is somehow restricted. There are two possible reasons for this occurrence. First, and most likely, is that the amide protons are involved in hydrogen bonding. Liu et al.³¹ showed that amide protons are involved in hydrogen bonding with carbonyl oxygen of adjacent amide unit in the growing chain. Another reason could be that the polymer, which is quite large, has the tendency to coil and some of the amide protons end up buried within the overall structure and not exposed to D₂O. The correlated spectroscopy (COSY) experiment, a two-dimensional NMR, of the polymer (data not shown) also confirmed that both of these peaks are correlated to each other, further evidence that both peaks belong to AM amide protons.

Assignment of the DADMAC signals were difficult because of the possibility of *cis-trans* isomerization of *H_a*, *H_b*, CH₃ (*H_c*), and *H_d* protons; however, low resolution and sensitivity of the spectra limits the identification of *cis* and *trans* isomers. Methylene protons (*H_d*) were seen at δ 1.29 ppm and can easily be differentiated from *H_f* protons of AM. Methylene protons (*H_{a,b}*) (at α -carbon to ring nitrogen) were assigned to a multiplet at δ 3.13–3.40 ppm. The flexibility and easy rotation of these protons makes it difficult to segregate them. Also the possibility of forming hydrogen bonding with the carbonyl oxygen of adjacent AM contributes to the complexity of the peaks. A peak at δ 3.02 ppm is assigned to the methyl protons (*H_c*), from the methyl groups from the nitrogen of DADMAC. Methine protons (*H_e*) were seen at δ 3.77 ppm as a low intensity broad peak which is also found buried under the guar backbone spectrum.

The most confusing and hence interesting point of the spectra is the emergence of 2 or 3 sets of multiplets between δ 5.6 and 6.5 ppm. These multiplets were not seen in the spectrum of pure guar gum confirming that they are not related to the guar backbone. A Heteronuclear Single-Quantum Correlation (HSQC) experiment of DADMAC-guar copolymer confirmed the multiplet at δ 5.65–5.87 ppm to be methylene (CH₂) protons and multiplet at δ 6.2–6.4 ppm to be methine (CH) protons. The COSY spectrum of guar-g-p(AM-co-DADMAC) copolymer sample shows that multiplets at δ 5.65–5.87 ppm and δ 5.97–6.12 ppm are correlated to a signal at δ 3.9 ppm, which is allocated to the guar backbone. This assignment of protons signals of the grafted chain is in line with the literature values.³³ Guar gum signals could not be identified clearly in the complex spectrum; however, the sequence of signals and their presence is very similar to what is reported in the literature.^{2,35} Crescenzi et al.² reported that the last peak in the ¹H-NMR of guar gum comes at δ 5.02 ppm and nothing was reported further downfield. Multiplets at δ 5.65–5.87 ppm and δ 5.97–6.12 ppm were also missing from the spectrum of AM-guar gum copolymer, further supporting the argument that DADMAC is contributing to them.

¹³C-NMR. Figure 3 shows the ¹³C-NMR spectra of the grafted copolymer. Signals at δ 37.6–40.2 ppm are assigned to (e) methylene carbons (inset Figure 3). The unresolved peaks at 44.5 ppm are assigned to methine (f) carbon, α -carbon to the carbonyl group of AM.

The peak at δ 182.2 ppm confirms the presence of amide carbonyl carbons (g). A broad peak at δ 27.9 ppm is allocated to methylene carbon (d), while the low intensity unresolved broad peak at δ 40.9 ppm is assigned to methine carbon (c), which is following the sequence and values reported by various authors.^{35–37} The methylene on carbon (b), α -carbon to DADMAC nitrogen which is buried under the complex structure of guar gum, can be assigned to the unresolved but sharp peak at δ 71.1 ppm which is consistent with literature values.^{34,38,39}

Experimental Results

The experimental results for the grafting and polymerization parameters for the various conditions are presented in Table II. Differences in percentage grafting (%G) were observed for the differing reaction conditions. The %grafting efficiency, both %GE1 and %GE2 yielded unrealistic results for polymers 2 and

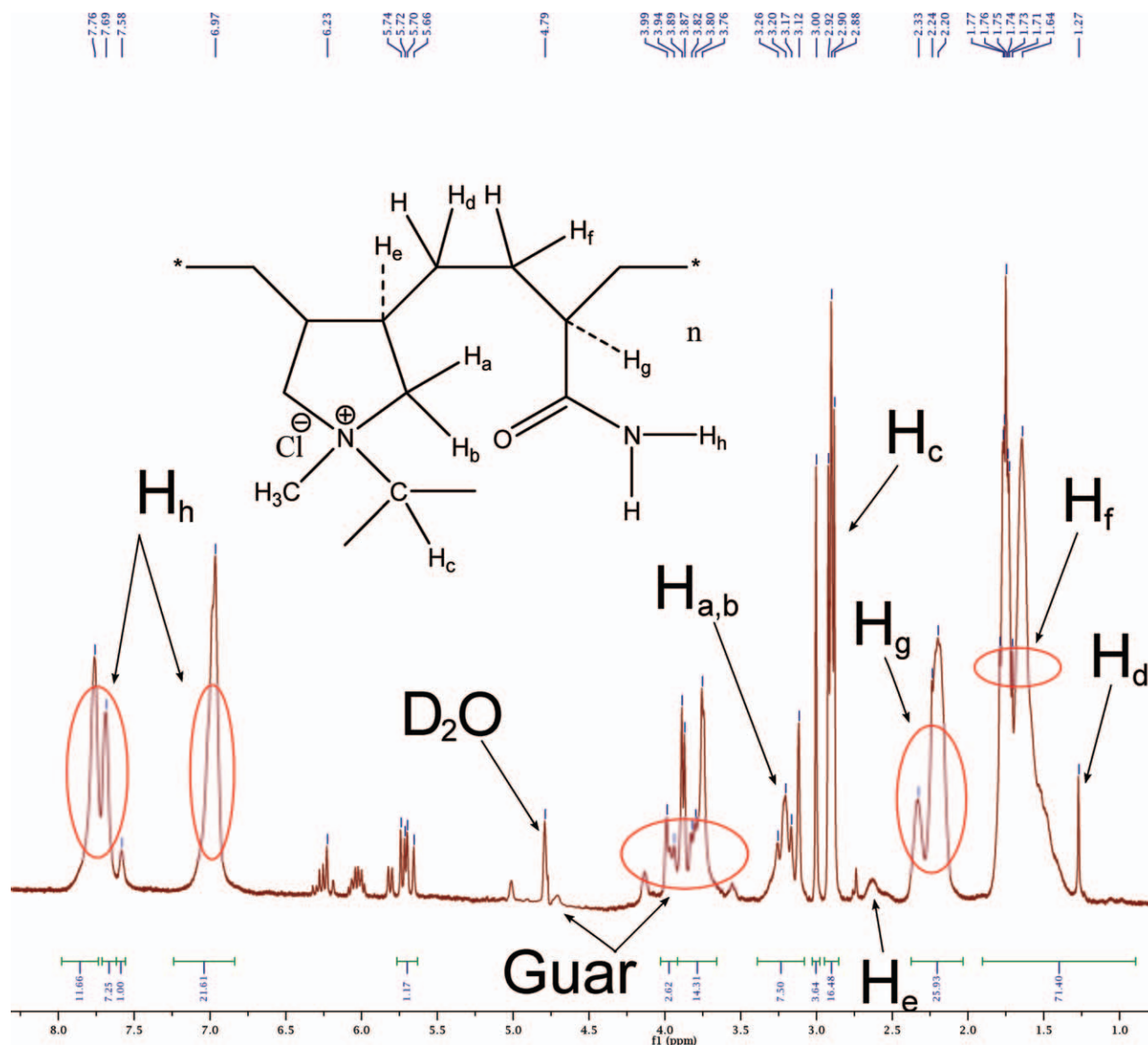


Figure 2. A typical $^1\text{H-NMR}$ spectra of guar-g-p(AM-co-DADMAC) grafted copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

4. The reason for this comes from how the values were calculated. Both eqs. (2) and (3) assumed that all the guar gum used was reacted which may not be true. In the case of polymers 2 and 4, the amount of purified grafted polymer was less than the amount of starting guar gum indicating that either some of the guar was lost in the synthesis procedure or was unreacted (which would have been lost in the workup). A new way of determining the grafting efficiency is required that determines the amount of guar reacted and calculates the amount of grafted material based on this value.

The highest % grafting (217 %) was found for polymer 1 (++++) (Table I) synthesized at 0.7M AM concentration, 60°C, and 1M acid concentration. This indicates that a considerable amount of material relative to the guar backbone was grafted. The grafting efficiency (%GE1) based on the total amount of

monomer added was 17.8% while the %grafting efficiency (%GE2) based on the amount of reacted monomer was 77%. The difference between the two results indicates that there was a considerable amount of unreacted monomer. The %MC also supports this as only 24.6% of the added monomer reacted and was grafted onto the guar backbone. There is evidence that some homopolymer (17.35%) was also formed in the reaction. These values are similar to the values reported in literature for similar systems.^{40,41}

The low %MC is likely due to the cerous ion [Ce (III)] being less capable of initiating radical formation for polymerization than Ce (IV). Although sulfuric acid was added to oxidize Ce (III) to Ce (IV) as recommended by Edgecombe and Norrish,⁴² other factors may have been inhibiting the oxidation of Ce (III) to Ce (IV) and the initiation of the radicals. Matthews et al.⁴³

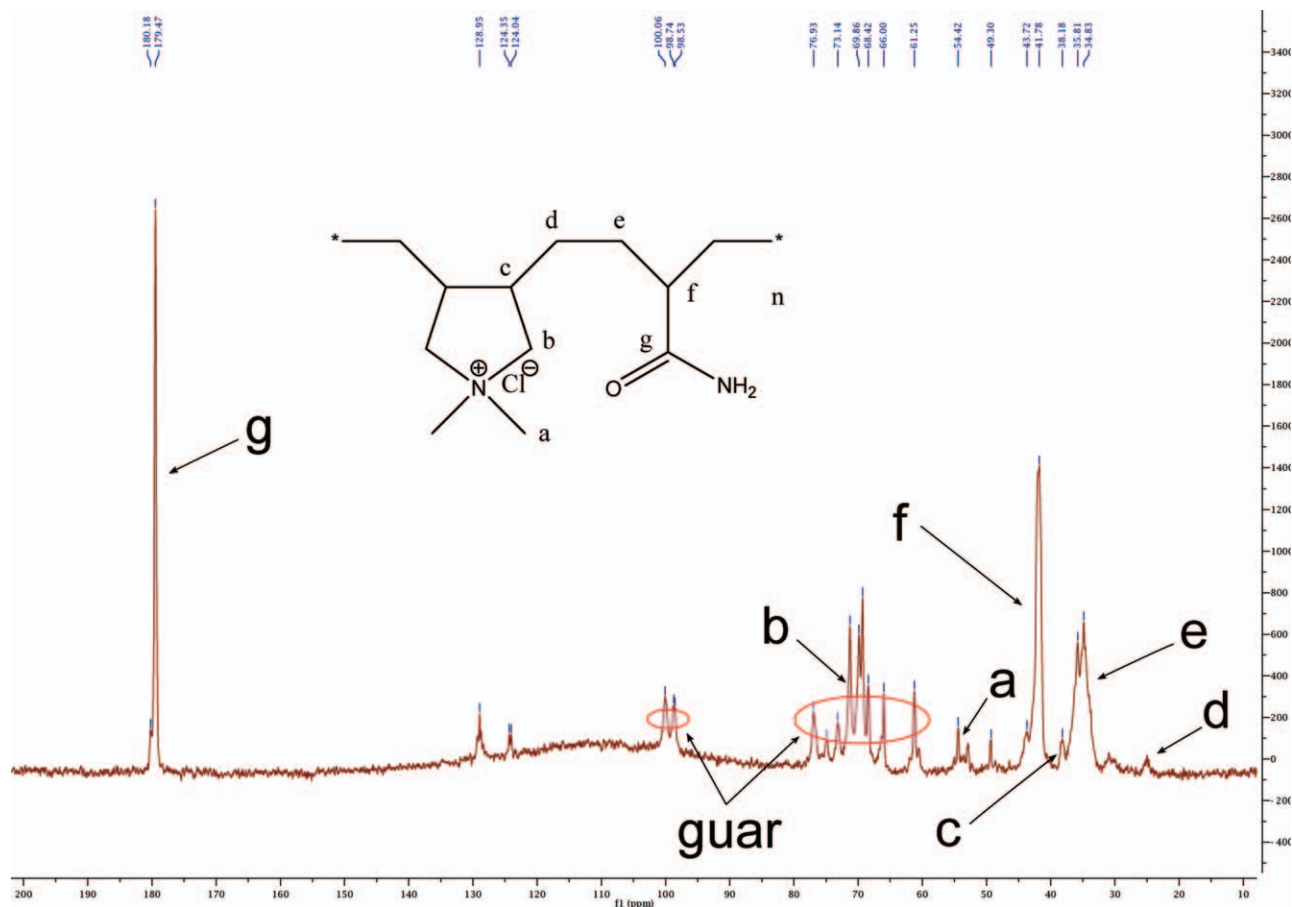


Figure 3. A typical ^{13}C -NMR spectra of the guar-g-p(AM-co-DADMAC) grafted copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reported that a low initial concentration of oxygen increased the initial rate of Ce (III) oxidation to Ce (IV). They found that later in the reaction oxygen production was enhanced resulting in Ce (IV) reaching a maximum and then decreasing to zero, suggesting that excess liberation of oxygen limited the oxidation of Ce (III) to Ce (IV) and radical formation. Excess oxygen

may have been produced in the reaction due to decomposition of the persulfate present in the reaction mixture. Kolthoff and Miller⁴⁴ conducted a mechanistic study of the decomposition of the persulfate ion in aqueous media and reported that a dilute solution of sulfur tetroxide decomposes rapidly to form oxygen and sulfuric acid.

Table II. Evaluation of Grafting Copolymerization Under Different Reaction Parameter Conditions

Polymer no.	Coded values ^a	% MC	% Grafting	% GE1	% GE2	% Homopolymers
1	+, +, +	24.6	217.1	17.8	76.5	17.4
2	-, +, +	0.3	-11.7	-1.5	-460.5	13.8
3	+, -, +	5.0	48.9	4.0	80.8	7.2
4	-, -, +	-0.4	-15.7	-2.0	552.8	13.2
5	+, -, -	5.7	63.4	5.6	98.2	0.7
6	-, -, -	2.2	0.9	0.1	5.5	13.5
7	+, +, -	14.2	170.5	14.0	98.7	0.8
8	-, +, -	5.3	16.1	2.0	39.8	17.3
9	0.3M, +, +	7.9	67.6	7.5	95.7	1.8
10	+, 45°C, +	11.1	91.8	7.5	70.3	16.8
11	+, +, 3.0M	18.6	207.3	17.0	92.7	5.0

^aCoded values represent the reaction variables in experimental design, AM concentration, reaction temperature, and acid concentration in that sequence.

Main Effects

The effect of each variable, main effect (concentration of AM, temperature, and acid concentration) and the interaction between the variables were investigated by constructing main effects and interaction effects plot. Figure 4 shows the plot for both the main and interaction effects for percentage grafting (%G). The main effects were calculated as the difference between average values at high reaction condition (coded as +) and the low reaction condition (coded as -) in the experimental design. The steeper the slope between the average of the positive and negative coded values, the greater the effect of that parameter on the reaction outcome irrespective of the connotation (direction of slope). It is evident from Figure 4 that the slope of the AM concentration (main effect) is steepest followed by the reaction temperature effect while the effect of the acid concentration is negligible.

Effect of AM. Effect of AM was studied at three different concentrations 0.15, 0.3, and 0.7 mole/L. It is evident from Table II that % grafting increased with the AM concentration. Similar results were observed for %MC and both %GE1 and %GE 2. The grafting values of all the polymers synthesized at 0.7M AM concentration (+), are higher than those synthesized at 0.15M AM concentration (-).

AM plays a very vital role in the grafting process. It is known that high monomer concentration favors the formation of acceptor-donor complexes between guar and monomers which triggers the grafting process.¹⁸ The insertion of AM between DADMAC units also increases the relative distance between DADMAC units which reduces the electrostatic repulsion between the charged units. The electrostatic repulsion hinders incoming DADMAC units thus resulting in low grafting. Because DADMAC is also bulkier than AM, it tends to increase the viscosity of the reaction mixture thus reducing the availability of backbone macro-radicals to the incoming monomeric units.

Four polymers each were synthesized with AM concentration 0.15 and 0.7 mole/L, and a constant DADMAC concentration (0.3 mole/L). It can be deduced from Table II that grafting values for polymers 2, 4, 6, and 8 are quite low and are even nega-

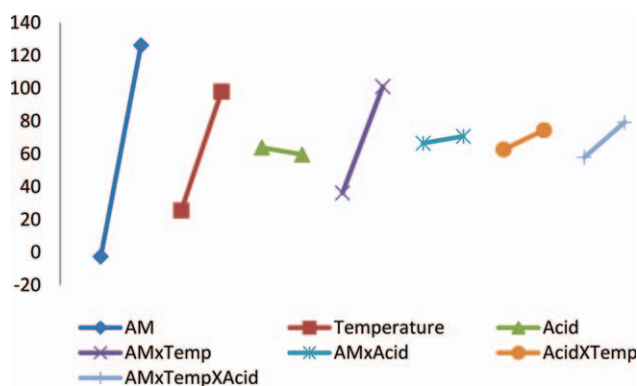


Figure 4. Plot of both main and interaction effects as means of percentage grafting. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tive in the case of 2 and 4. These are the polymers synthesized at 0.15M AM concentration. The negative results arise because the final yield is less than 1 g of guar gum added. Equations (1)–(4) assume that all the guar added has reacted. At low reaction temperatures (30°C), foaming occurred which resulted in loss of guar gum onto the walls of reaction flask. Therefore, in reality not all the guar gum reacted and this explains the yields of less than 1 g, which was the amount of starting material. This also along with the fact that not all the added monomer actually took part in the reaction helps to understand the unrealistic numbers of %GE1 and %GE 2. It was also noted that % homopolymer (>13%) was higher and also consistent throughout polymers 2, 4, 6, and 8, synthesized at 0.15M AM concentration. This is because AM radicals are not able to access the guar backbone to facilitate grafting. This can be related to the fact that DADMAC present in the reaction mixture is limiting AM exposure to guar. This promotes AM homopolymerization instead.¹⁸

Effect of Temperature. Grafting reaction was studied at three different temperatures 30, 45, and 60°C. It can be seen from Table II that, as the reaction temperature increases from 30 to 60°C, %G, %MC, %GE1, and %GE2 also increases. This effect is attributed to the fact that the rate of radical formation increases with an increase in temperature. This results in higher grafting and also promotes diffusion of monomers onto the backbone,²⁵ as a result of swelling of the backbone.

Viscosity of the reaction solution is known to reduce with an increase in temperature, facilitating greater access of monomers onto guar backbone. Casas et al.¹⁵ reported that at low reaction temperature not all guar molecules are dissolved and hence results in lower grafting. This would explain the negative grafting values for polymer 4 and very low grafting for polymer 6.

Effect of Acid Concentration. The grafting reaction was carried out by varying the sulfuric acid concentration from 0.5 to 3 moles/L. No clear trends are evident in the results for acid concentration. It was believed that acid concentration would improve the efficiency of the reaction through promoting primary radical formation.^{16,17} The results obtained in this work indicate that other variables may be dominating the reaction.

Interaction Effects

There are two types of interaction effects considered in this study: three 2-way interaction (concentration of AM × reaction temperature), (concentration of AM × acid concentration), and (reaction time × acid concentration) and one 3-way interaction (concentration of AM × reaction temperature × acid concentration). The steeper slope of (concentration of AM × reaction temperature) indicates that this interaction has a stronger effect on the reaction followed by the other 2-way interactions of (concentration of AM × acid concentration) and the 3-way interaction of (concentration of AM × reaction temperature × acid concentration).

AM Concentration × Temperature. It can be seen from Figure 4 that the 2-way interaction effect between AM concentration and temperature has the steepest slope amongst the interaction effects. This is not unexpected especially when main effects of

Table III. Results for all the Effects on %G, %GE1, %GE2, %MC, Charge, and Intrinsic Viscosity Measurements

Effects	% G	% GE1	% GE2	% MC	Viscosity	Charge
AM	128.8	8.9	54.2	10.2	-0.8	165.5
Temperature	72.4	6.2	-245.7	7.6	-0.5	198.9
Acid	-4.3	-0.9	1.9	0.3	0.8	-97.5
AM × temp	64.8	5.2	243.8	5.8	0.5	129.1
AM × acid	4.2	0.2	-21.6	3.9	-0.1	86.5
Acid × temp	11.7	0.8	-263.1	1.9	-0.1	-86.2
AM × temp × acid	21.3	2.0	260.7	3.1	0.7	-1.9

AM concentration and temperature have considerable effect on the reaction (Table III). However, from Figure 5 which is a normalized plot for outliers, it is evident that none of the interactions are considerably important, as all the values fall within the 95% confidence level.

Outliers are the parameters or effects which govern the outcome of the reaction. To reach the optimum these particular effects are crucial and should only be considered and manipulated to reach the optimum. The most important information extracted from Figure 5 is that there is evidence of interaction amongst the factors which could not be evaluated using the traditional method of altering one parameter at one time. Morgan⁴⁵ states, "Main effects must only be interpreted individually if there is no evidence of interactions." Although none of the interaction effects were significant in this study, their presence supports the argument about their existence (interaction effects) and that they must be considered while designing the experiments especially when demonstrating the effect of reaction parameters on reaction outcome.

Table III shows the data of the various effects (both main and interaction effects) for %grafting efficiency 1 (%GE1), %GE2, %MC, charge on the polymer, and intrinsic viscosity. It is noticed that both these coefficients show a similar trend as %grafting (%G), the only difference is in the behavior of acid which shows a positive slope for %MC. However, calculation for the main effects show that slope of acid concentration is negligible (Figure 4).

Physical Properties of the Grafted Copolymers

Viscosity Measurements. The intrinsic viscosity $[\eta]$ of a polymer is known to be directly related to its morphology and mo-

lecular weight as shown by Guth and Mark⁴⁶-Houwink⁴⁷ The relationship is shown in eq. (7)

$$[\eta] = KM^a \quad (7)$$

where K and a are constants; M is the mass of the polymer.

It is clear from eq. (7) that $[\eta]$ and molecular weight are directly proportional to each other.⁴⁸ Linear polymers are known to have a higher viscosity as compared with their branched counterparts with the same molecular weight. The reason for this is that linear polymers have a higher hydrodynamic volume in solution; the longer the chain, higher the intrinsic viscosity and vice versa.⁴⁹ It is also known that $[\eta]$ depends on some key parameters including temperature¹⁵ and solvent interactions.^{50,51} There is a limitation to the Mark-Houwink equation [eq. (7)], as it requires both the constants to determine the molecular weight from $[\eta]$, and K and a are not known for the polymer synthesized in this study. In this study, no clear trend in the viscosity with varying reaction conditions is observed.

Even though no significant trends are noticed, it can be observed from the graph shown in Figure 6, that all the polymers synthesized at 1M acid concentration tend to have $[\eta]$ value greater than 1.5 and all the polymers synthesized at acid concentration of 0.5M have $[\eta]$ values less than 2.0. So it can be assumed that at higher acid concentrations, polymer chains are more linear and longer than polymers synthesized at lower acid concentration, which would have more branched structure, but nothing can be confirmed from this study.

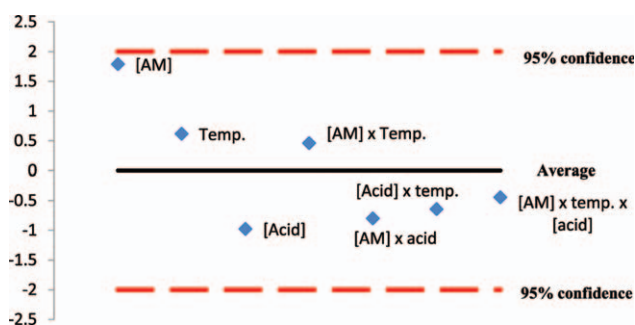


Figure 5. Normalized plot of all the main and interaction effects for various reaction parameters to calculate the outliers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

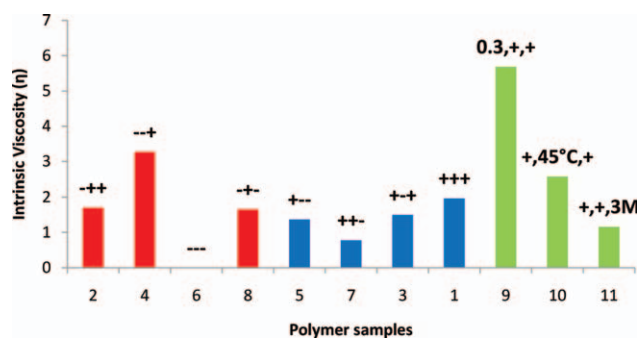


Figure 6. Intrinsic viscosity of polymer samples in water. Data labels in the figure show the coded values under experimental design. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

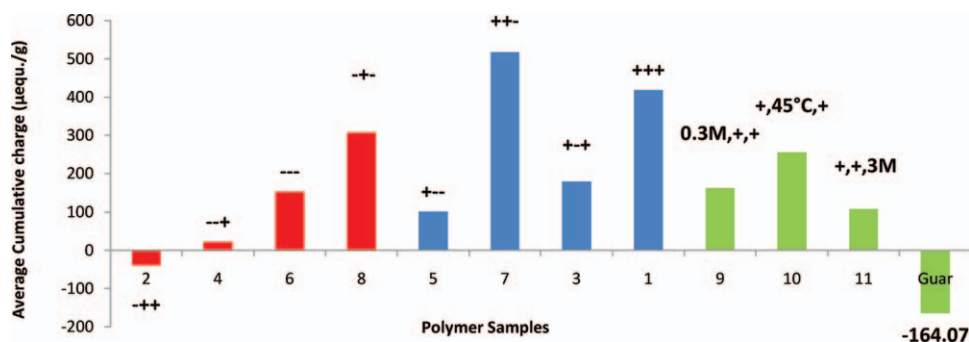


Figure 7. Plot of distribution of average cumulative charge on different polymers in $\mu\text{equ./g}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

It is observed from the main effects calculations, shown in Table III, that concentration of acid has the highest value of 0.84. This suggests that with increasing acid concentration, intrinsic viscosity of the sample increases. However, the effect is not very significant; also no significant interaction effect was noticed from the calculations (Table III).

Charge Measurements. Charge measurements were carried out to investigate the effect of different reaction conditions on the overall charge of the polymer (Figure 7). Because there is only one contributor of cationic charge in the whole make up of the polymer i.e., DADMAC, it is obvious that altering charge signifies changes in the grafted chains. Aqueous guar gum was shown to have a high negative charge of $-164 \mu\text{equ./g}$. This was an important result to know to understand the extent of the contribution of the charged copolymer to the overall charge of the whole polymer for the different reaction parameters. It is evident from the data that all the polymers synthesized at 60°C have higher values compared with their counterparts synthesized at 30°C , keeping the other parameters constant. Main effects calculation (shown in Table III) confirmed this observation, as the highest value is obtained for the temperature effect. This result is in line with the work of Huang and Reichert⁵² on polymerization of DADMAC. Polymers 6 and 8, 5 and 7, and 3 and 1 follow this trend, showing that more DADMAC is grafting at 60°C . This hypothesis is supported by the charge value on polymer 10, synthesized at 45°C , which falls comfortably between the average charge value of four polymers synthesized over this temperature and four polymers synthesized at 30°C . This could be because with the increase in temperature during the synthesis, the viscosity of the guar gum backbone reduces and the polymeric guar backbone swells exposing greater surface area for grafting of DADMAC.

The only exception to the trend is polymers 2 and 4 whose low viscosity values indicate low DADMAC grafting on the backbone. The negative charge on polymer 2 does not indicate an absence of DADMAC in the graft copolymer, as the presence of DADMAC was confirmed in the NMR studies, it just shows that the overall grafting is quite low in this polymer. Both polymers 2 and 4 were synthesized at low AM concentration ($0.15M$) which would result in higher overall DADMAC concentration in the overall reaction mixture, yielding greater repulsion between DADMAC units and hence low GE and higher homopolymer formation.

CONCLUSION

Graft copolymerization of guar-*g*-(AM-*co*-DADMAC) was achieved in this study under complex initiation system of cerous sulphate and potassium persulfate. A direct relationship between the three reaction variables studied (concentration of AM, reaction temperature, and concentration of acid) and grafting, %MC and %GEI were observed. For the conditions investigated, the highest degree of grafting (217%) was achieved at $0.7M$ AM concentration, 60°C reaction temperature and $1M$ acid concentration. Low AM levels were found to result in low grafting and monomer conversion. It was found that charge on the synthesized polymers increased with the increase in reaction temperature. No relationship with the degree of grafting was observed. It can be concluded from this study that properly designed experimental design is a better technique than the traditional approach of changing one parameter at a time; to study the effect of reaction parameters on its outcome. Presence of interaction effects in graft copolymer synthesis was demonstrated for the first time through this study. This work can be taken as a platform to develop a model for the future development in the area of graft copolymerization of polysaccharides. To achieve the reaction optimum a carefully designed experimental design such as centre composite design could provide the best solution under which all the possible effects which govern the fate of reaction outcome are considered and studied.

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