

Libraries of modified polyacrylamides using post-synthetic modification

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ABSTRACT: Polyacrylamide-based (PAM) polymers are the most widely used synthetic water-soluble polymer so they are applied in a range of industries. However, they suffer from a number of limitations which requires the development of synthetic routes that can accurately control polymer structure and hence function. This study describes a carbodiimide mediated coupling reaction (CMC) that is used to generate modified polyacrylamide (PAM) including hydrophobically modified water-soluble polymers (HMWSP). The reaction proceeds efficiently in water and does not require organic solvents or high temperatures. The approach is flexible due to the efficiency of the CMC reaction allowing for accurate control over polymer structure and function. This is confirmed using acid-base titration, spectroscopy, viscometry, and rheology. The viscosity of the polymers varies over a broad range with those containing larger hydrophobic group (dodecyl) showing the highest viscosity. The hydrophobicity of the pendent group determines how it influences viscosity and using this new synthetic approach polymer with the same molecular weight can be compared. Linear hydrocarbon pendent groups are more hydrophobic than the cyclic versions resulting in higher viscosity. However, the spatial arrangement of the pendent group (linear or cyclic) also affects the viscosity at higher pendent group contents. The number of modified PAMs that can be generated is expansive because the approach works with a number of different functional groups and base polymers. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42797.

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INTRODUCTION

Synthetic water-soluble polymers have been used for a number of years as viscosity enhancers in a broad number of industrial applications including paint formulations, foods, water purification, pharmaceuticals, cosmetics, drilling fluids, enhanced oil recovery, hydraulic fracturing and drag reducing agents.^{1–10} Polymers based on acrylamide (PAM) are the most extensively studied group of synthetic water-soluble polymers so they are commercially available in large quantities. Despite the widespread use of PAM-based polymers they often exhibit a loss of performance when subjected to high temperatures, shear, or increasing ionic strength. As such there is a need for alternative routes to control the structure of the polymers to enhance performance.

These issues can be overcome by synthesizing specialized classes of PAM-based polymers such as hydrophobically modified water-soluble polymers (HMWSPs). HMWSPs are ionic or neutral polymers containing a small amount of hydrophobic groups (up to 5 mol %).⁸ The hydrophobic groups impart unique

properties as they tend to associate with each other forming intra- or intermolecular aggregates which causes a significant increase in the viscosity of the solution.^{1,4,11} This behavior is dependent on the polymer concentration, for example, in dilute solutions intramolecular associations between the hydrophobic groups dominate. This results in contraction of the polymer and viscosity reductions of the solution. Conversely, at high concentration intermolecular associations lead to formation of a physical network which causes an increase in viscosity.¹² The solution viscosity is also dependent on the molecular structure, solvent, ionic environment and temperature. As well as unique viscosifying properties these polymers possess other advantages over PAM-based polymers (without hydrophobic groups) including improved stability to salt and mechanical degradation. This leads to a number of applications in water treatment, oil recovery, pharmaceuticals, cosmetics, and food.⁴ There are a number of disadvantages associated with HMWSP in terms of synthesis because the hydrophilic and hydrophobic groups are mutually incompatible which requires complex processes or

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organic solvents. In addition, HMWSP are often slow to dissolve which hinders their widespread application which can be overcome by hydrolysing the HMWSP to generate carboxylate groups that can improve solubility.¹¹

In general for PAM-based polymers (with and without hydrophobic groups) there is need for new routes that accurately control structure, composition, and molecular weight whilst minimizing toxic residues. In addition, the synthesis must be scalable because polymers of this type find widespread application. However, this requires synthetic protocols that allow accurate placement of functional groups in high yields. There are currently two routes that are used to synthesize these polymers involving free-radical copolymerization of target monomers, or modification of an existing water-soluble polymer (post-polymerization modification).^{11,13–16} Free-radical polymerization involves reacting acrylamide with a co-monomer(s) to generate the target structure. This method is used extensively but there are a number of limitations including: unequal incorporation of target groups; lack of monomer availability for complex structures; the use of acrylamide monomer which is a potent neurotoxin; difficulty in accurately controlling molecular weight; and oxygen inhibits the reaction. In addition, for HMWSP specialized polymerization techniques are required due to the incompatibility of the hydrophilic and hydrophobic monomers.¹¹ This includes heterogeneous, inverse emulsion, microemulsion, precipitation, and micellar free-radical copolymerization. There are issues with all of these methods in terms of compositional drift in the resulting polymers because the hydrophobic groups exist as blocks. For example, Valint and Bock¹⁷ showed that block and random distributions of hydrophobic groups demonstrate large differences in terms of rheology. However, when compared to homopolymers and random copolymers of similar composition and molecular weight the block configuration shows increased viscosity.^{17–19} A further issue with free-radical copolymerization is the large differences in molecular weight and molecular weight distribution between samples.^{11,20} Therefore it is challenging to make meaningful comparisons between samples and to target controlled structures. For example, the aqueous solution properties can be influenced by the architecture of the polymers including molecular weight, size or nature of the hydrophobic groups.²¹

The second method to synthesize PAM-based polymers is through post-synthetic modification of existing polymers. For HMWSP this method overcomes many of the issues by generating HMWSP with a more statistical arrangement of hydrophobic groups because of the homogeneous reaction mixture.^{18,22} Commercially available polymers can also be used as precursors which assists with large scale synthesis. Post-synthetic modification also allows for more accurate control over the incorporation and structure of the hydrophobic groups. In addition, the molecular weight of the polymers is constant across large groups of modified polymers.^{3,11,16,23} Moreover, by carrying out an additional hydrolysis step¹¹ of the HMWSP additional carboxylic acid groups can be generated. This has also been reported for polymers prepared by micellar free-radical copolymerization.⁷ This is advantageous because the carboxylic acid groups decrease dissolution time which overcomes a barrier to implementation of HMWSP. The groups are also charged which increases the repulsion and hence

the hydrodynamic volume of the polymer chain and the solution viscosity.

There are issues with post-synthetic modification of polymers which include the need for efficient chemistry that can accurately incorporate target functional groups (e.g., hydrophobes). In addition, post-synthetic modification is typically carried out using non-aqueous transformations (i.e., using DMSO^{3,11} or NMP²³) at elevated temperatures.^{11,16,23} These conditions ensure that the reactions are homogeneous and proceed to high conversions. However, the resulting polymers are typically applied as aqueous solutions so after the modification reaction additional purification steps are required.

Overall there is a need for new synthetic routes for PAM-based polymers that can accurately and efficiently control the placement of functional groups (including hydrophilic and hydrophobic) whilst maintaining the same molecular weight across different samples. Ideally the route should also minimize purification steps, proceed under mild conditions, be tolerant to impurities, and eliminate the use of toxic monomers or solvents. Recently, we demonstrated that a carbodiimide mediated cross-linking (CMCL) reaction could be used to generate polyacrylamide-based hydrogels.²⁴ Carbodiimide coupling is a nontoxic transformation²⁵ that facilitates the formation of an amide linkage between a carboxylic acid and an amine group and can occur in aqueous media using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC). It has also been used to modify polymers^{26,27} and form hydrogels,²⁴ however, it has not been used for aqueous-based generation of acrylamide-based HMWSP.

The aim of this study was to investigate if a carbodiimide mediated coupling reaction (CMC) could be used as a new method for post-synthetic modification of a polyacrylamide (PAM) polymer in water. Specifically the acrylic acid groups in a commercially available polyacrylamide-co-acrylic acid polymer (PAM-co-AA) were reacted with EDC. The EDC groups were then replaced with NHS which activated the PAM-co-AA to react with a broad range of different amines. Using this method functional groups were added to the PAM-co-AA from short chains cyclic groups through to hydrophobic moieties (e.g., C₁₂ groups) to generate a PAM-based library. This route uses a single base polymer for generating all of the modified polymers which removes variations in molecular weight. The modification occurs along the chain of the polymer thus avoiding compositional drift along the polymer. Detailed characterization of the resulting polymers was carried out and is also presented. In addition, cross-linking studies are also presented looking at forming a hydrogel from one of the modified polymers from the library.

EXPERIMENTAL

Materials

All of the chemicals were used without further purification. Purchased from Sigma Aldrich: polyacrylamide-co-acrylic acid partial sodium salt (PAM-co-AA), Mw 520,000, *M_n* 150,000, typical acrylamide level 80%; N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC, commercial grade); N-hydroxysuccinimide (NHS, 98%); isopropylamine (isoprop, 99%); cyclopropylamine (cycloprop, 98%); cyclobutylamine (cyclobut, 98%); cyclopentylamine (cyclopent, 99%); cycloheptylamine

Table I. Representative Synthesis Conditions Based on 5 mL of a 15 w/v % PAM-co-AA Solution

Activated polymer (%) ^a	Activators		Primary amines ^b							
	EDC (g)	NHS (g)	Isoprop (μL)	Cycloprop (μL)	Cyclobut (μL)	Cyclopent (μL)	Cyclohept (μL)	Cyclooct (μL)	C ₇ (μL)	C ₁₂ (mg)
1	0.0201	0.012	9.1	7.28	9.0	10.1	13.2	14.2	12.0	19.3
2	0.0399	0.024	18.2	14.6	18.0	20.2	26.3	28.5	24.0	38.7 ^{e,f}
5 ^c	0.1005	0.06	45.4 ^d	36.4 ^d	45.0 ^d	50.4	65.8	71.1	60.1 ^g	96.6 ^g
10 ^c	0.201	0.12	90.8	72.8	90.0	100.8	131.6	142.2	120.1 ^g	193.3 ^g
15 ^c	0.300	0.18	136.2	109.2	135.0	151.2	197.4	213.3	180.2 ^g	289.9 ^g
20 ^c	0.399	0.24	181.6	145.6	180.0	201.6	263.2	284.5	240.3 ^g	386.5 ^g

^aMol % of polymer repeat units activated with EDC and NHS, 20 mol % is the maximum because the polymer contains 20% AA, the molar ratio 1AA : 1EDC : 1NHS.

^bPolymers are denoted as PAM-amine-x, where x represents the theoretical modification percentage of the polymer by the requisite amine.

^cTo maintain a homogeneous solution after adding the amine at a concentration higher than 5% it was necessary to add THF (0.5–1.5 mL) to the final solution apart from systems marked (d).

^ethis system was used for further reaction to form a hydrogel by cross-linking through remaining carboxylic acid groups.

^fPAM-C₁₂-2 was used for the shear thinning rheology test.

^gpolymers are insoluble in distilled water.

(cyclohept, 99%); cyclooctylamine (cyclooct, 97%); heptylamine (C₇, 99%), dodecylamine (C₁₂, 99%), 1,2-diamino ethane (EDA, >99%); and potassium hydrogen phthalate (KHP, ≥99.95%). Ethanol absolute (ACS) and potassium hydroxide (KOH, 85%) were purchased from Merck, tetrahydrofuran (THF, HPLC grade) from Scharlau and deuterium oxide (D, 99.9%) from Cambridge Isotope Laboratories Inc.

Preparation of Modified Polymers

The reaction was carried out in open vials in the presence of oxygen at room temperature. EDC was dissolved in distilled water and added to an aqueous solution of PAM-co-AA (15 w/v %), the resulting solution was mixed and the viscosity increased. NHS dissolved in distilled water was then added and the mixture was vigorously mixed. The reaction was left to proceed for a further 3 min; this process activated the polymer to post-synthetic modification. For this study a stock solution of the activated polymer was prepared which was divided into different samples. After this time the requisite amine was added using a syringe (note: isopropylamine and cyclopropylamine are volatile) and the solution was mixed. Representative synthesis conditions are shown in Table I for a library of modified PAMs prepared at one polymer concentration (15 w/v %), with eight primary amines, at six concentrations. Most of the resulting polymers are soluble in distilled water and the exceptions are indicated in Table I, these are polymers that have been modified with larger groups (C₇ and C₁₂) at high percentages of modification (>5% activation).

The molar ratio was 1AA : 1EDC : 1NHS : 1 amine for all samples prepared. For modification levels greater than 5 mol % (determined by the amount of EDC, NHS, and amine) a few drops of THF were slowly added to ensure that the final solution was homogeneous. The resulting polymers were purified by re-precipitating into ethanol, followed by drying under vacuum at 50°C, and then freeze dried.

Hydrogel Synthesis from Modified PAM

A hydrogel based on a 2 mol % dodecylamine modified polymer (PAM-C₁₂-2, Table I) was generated by first functionalizing the polymer and subsequently cross-linking. For the hydrogel 0.798 g EDC and 0.48 g NHS was dissolved in 1 mL of distilled water respectively. Then a 10 mL solution of PAM-co-AA (15w/v %) was activated by EDC. After 3 min, NHS was added to the solution and was left for a further 3 min, the final solution is a polymer with full activation (20 mol %). The functionalization was carried out with the addition of 0.0772 g dodecylamine (C₁₂) dissolved in 0.1 mL THF and 0.5 mL of distilled water, the solution was thoroughly mixed. After 3 minutes 0.108 g of 1,2-diaminoethane (EDA) dissolved in 1 mL of distilled water was added to the solution to cross-link the polymer through the remaining activated carboxylic groups that were not reacted with dodecylamine (18 mol %).

Characterization

Titration of the Polymers. The AA content of the polymers was measured by acid-base titration. The solutions were prepared with approximately 0.4 g of purified polymer. The polymers were left for 24 h at room temperature to ensure they were dissolved. The solutions were then titrated against KOH 0.01N which had been previously standardized with KHP. Phenolphthalein in ethanol 1 wt % was used as the indicator. The acid number (mg KOH/g of sample) was calculated using the eqs. (1) and (2), where:

$$AN = \frac{Vol_{KOH} \times N \times 56.1}{W_{polymer}} \quad (1)$$

Vol_{KOH} is the volume of titrant, N is the molar concentration of titrant, 56.1 is the molar mass of KOH, and W_{polymer} is the mass of polymer in grams.

$$N = 1000 \frac{W_{KHP}}{204.23 \times Vol_{KOH}} \quad (2)$$

Viscosity Determination of Polymer Solutions. The viscosity measurements were conducted on a vibrational viscometer

(Vibro Viscometer, SV-1A), at $25 \pm 0.1^\circ\text{C}$, using distilled water as standard for calibration. A water jacket was used in conjunction with a refrigerated bath and heat circulator (Thermoline Scientific) to ensure that the samples remain at a constant temperature during the measurements. The polymer solutions were prepared by dissolving the polymers in distilled water for 24 h at room temperature. The samples were left in the system for 15 minutes before the measurement to ensure that the temperature had equilibrated.

Nuclear Magnetic Resonance. ^1H NMR spectroscopy was performed on a Bruker Av400 NMR spectrometer using deuterium oxide (D_2O) as solvent and ^{13}C NMR spectroscopy was performed on a Bruker Av500 NMR spectrometer with a 10 mm autotuning and matching broad band observe probe. Samples with concentration of 50 wt % $\text{H}_2\text{O}/\text{D}_2\text{O}$ (9 : 1) were held at 50°C inside the probe. An 83° pulse was used with inverse-gated ^1H decoupling using a bilevel waltz-16 decoupling sequence. The acquisition time was 1.08 s and the relaxation delay was 10.0 s, the sum of 11.1 s being greater than 53 the longest T1 measured using an inversion recovery sequence. The data were zero-filled once and exponential multiplication using 5 Hz line broadening was applied prior to Fourier transformation. The NMR is used for qualitative analysis because it is challenging to accurately determine composition for these polymers using NMR.

Rheology. Rheology was performed using a HR-3 Discovery Hybrid Rheometer (TA Instruments) and a smart swap recessed concentric cylinder geometry with a cup (radius 15 mm) and rotor (radius 14 mm, and height 42 mm). The gap between the bottom of the cup and rotor was set at 4 mm and heating was achieved using Peltier heaters. *Hydrogel:* The PAM-co-AA base polymer was activated with EDC and NHS, then the cross-linker was immediately added. 12 mL of the resulting solution was quickly loaded into the measuring geometry. A lid was used to cover the cup to minimize evaporation of the water and to further prevent this mineral oil was poured on the top of the solution and as a result no shrinkage of the hydrogels was observed. Cross-linking was monitored as a function of time and the oscillation frequency was 1 Hz and strain was kept at 0.01%. The experiments were performed for 19.5 h to ensure the cross-linking reaction was complete which was determined as the plateau in the modulus which occurred before 19.5 h. Shear thinning testing was performed in a flow sweep mode with the same configuration. The shear rate is from 0.01 to 3500 1/S, using a solution of 12 mL, 5 wt % of PAM-C₁₂-2 (Table I) and a solution of PAM-co-AA base polymer (5wt %) were tested.

RESULTS AND DISCUSSION

The polymers synthesized in this work were obtained by post-synthetic modification of a precursor PAM-co-AA with various amines. This was achieved using a CMC reaction resulting in a library of modified PAM-based polymers including hydrophobically modified water-soluble polymers (HMWSP). All of the polymers possess the same molecular weight (M_w 520,000, M_n 150,000) but with different functional groups incorporated at controlled concentrations. In the following sections the synthesis and characterization of the polymers is discussed.

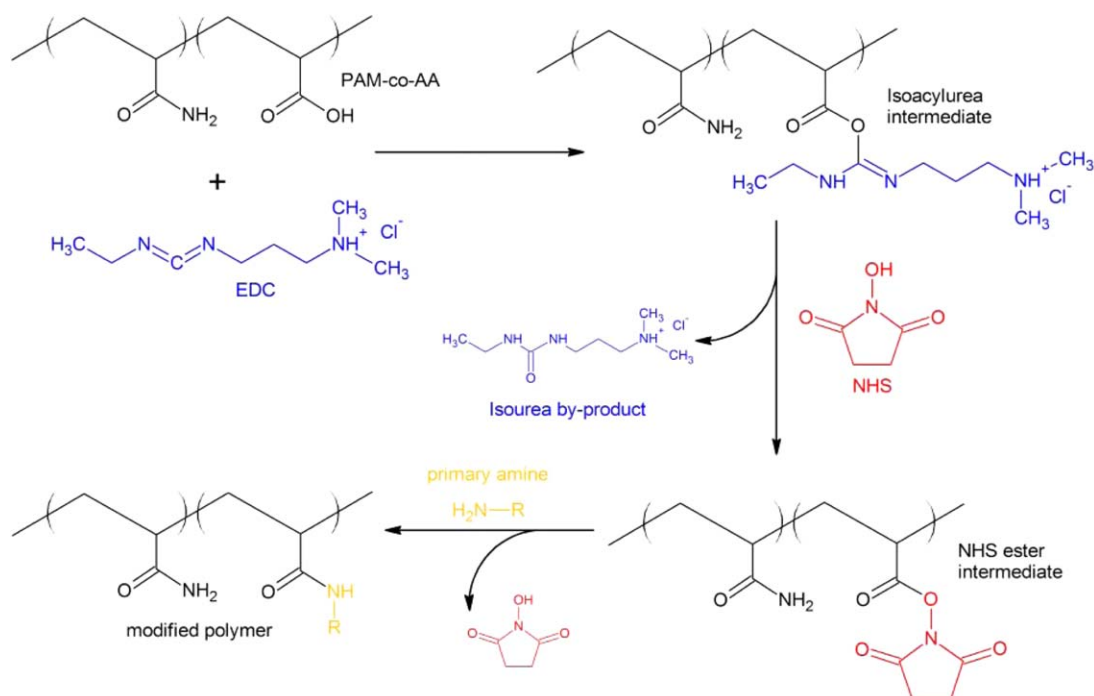
Synthesis of Modified PAM-libraries

Prior to modification of the PAM-co-AA base polymer it was fully characterized to determine the concentration of the AA groups as discussed previously.²⁴ The base polymer contains 20 mol % of AA groups that can be used for modification. The CMC reaction used EDC and N-hydroxysuccinimide (NHS) which are routinely used to activate carboxylic acid groups to react with amines to form an amide bond (Scheme 1). The EDC reaction results in the formation of an acylurea which undergoes further reaction with NHS to form a more stable NHS intermediate. This NHS-modified group readily reacts with amines to form an amide bond.²⁸ The reactions proceeded at room temperature in aqueous solution and were carried out in open vials. It is worth noting that the side products from the reaction are isourea and NHS so carbodiimide coupling is regarded as a nontoxic transformation.^{25,29} The primary hazards associated with the amines used to modify the polymers is their corrosiveness, however, as we discuss in the following sections unreacted amines were not detected in the modified polymers. In contrast, free-radical copolymerization uses a number of reagents that can all contribute to toxicity including acrylamide, initiators, and co-monomers. Therefore, the CMC reaction offers an alternative route to generate modified PAM-based polymers that eliminates the use of toxic monomers.

As can be seen from the reaction mechanism the extent of modification of the polymers can be controlled simply by changing the concentration of the EDC, NHS, and amine. The maximum level of modification is controlled by the amount of AA in the base polymer. The polymer used in this study contains 20 mol % AA which is the maximum level of modification. However, there are a broad range of different base polymers that are commercially available or can be synthesized that could be used with this route. For HMWSP the amount of incorporation of hydrophobic groups is typically less than 5 mol % which can be easily controlled using the CMC reaction. However, HMWSP display slow dissolution rates often taking a number of days to dissolve, which impedes their implementation. The solubility of HMWSPs decreases with hydrophobe content, molecular weight, and hydrophobe chain length. This limits the maximum hydrophobe content that can be introduced into a HMWSP. This can be overcome by further hydrolysis of the acrylamide in HMWSP^{7,11} to generate charged carboxyl groups to impart better solubility in water (as well as increased viscosity). The resulting polymers are terpolymers containing three structural units including acrylamide, charged carboxyl, and hydrophobic groups. Using the CMC reaction structurally analogous terpolymers were readily generated when <20 mol % modification was carried out due to the carboxyl groups that had not been activated with EDC and NHS which is an important advantage of this route. As discussed in the following section the dissolution rates for the polymers synthesized in this study were less than 24 h.

Characterization of Modified PAM-Libraries

To determine if the reactions outlined in Table I were successful detailed characterization of the polymers was carried out including titration of the acid groups, NMR spectroscopy, and viscosity measurements. It is challenging to accurately determine the percentage of modification using NMR spectroscopy because



Scheme 1. Reaction schematic used for the synthesis of modified PAMs where PAM-co-AA (shown in black) reacts with EDC (shown in blue) and NHS (shown in red) to form an activated polymer (NHS ester intermediate), the NHS is readily replaced with primary amines (shown in yellow). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the chemical shifts of key groups in 1H NMR overlap and ^{13}C NMR has limited quantitative accuracy. As such titration was used to correlate the percentage of modification and Figure 1 shows the acid number for the polymers as determined using acid-base titration. The acid number represents the mass of KOH that is required to neutralize one gram of the polymer.

The acid number for the base polymer is the highest as shown in blue. As the percentage of modification increased (by using higher concentrations of EDC, NHS, and amine) the acid

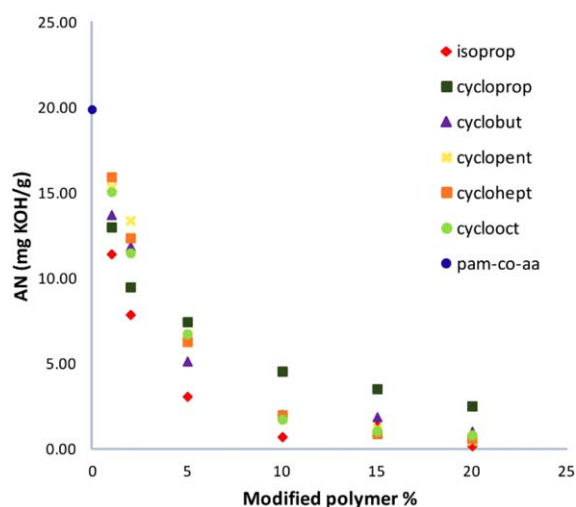


Figure 1. Acid number determined by titration for the PAM-co-AA base polymer and six different functional groups at six different levels of incorporation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

number decreased. This is due to consumption of the AA during the modification reaction so the higher the percentage of modification the less AA is present. The decrease is seen for all the different amine functional groups that were used. The trend for this reduction is also the same for each functional group. However, the acid number is not the same at one percentage of modification across the different functional groups. This is due to inaccuracies when the activated polymer solution was split, to improve the accuracy the samples can be prepared separately. In addition, the reactivity of the amines towards the NHS-modified intermediate is different. Alternatively, the solution properties of the resulting polymers vary substantially and the accessibility of the carboxyl groups could be different particularly at elevated pH as the polymers could be contracting. Therefore, further studies were carried out using NMR spectroscopy to reinforce the successful modification of the polymers.

1H NMR for the base polymer shows the characteristic peaks for PAM-co-AA and the chemical shifts are highlighted in Figure 2. The spectra for isopropylamine (isoprop) and a mixture of the base polymer and isopropylamine are also shown as controls. The peaks for the isoprop can be clearly seen in the mixture with the base polymer. The base polymer was then reacted with isopropylamine using the CMC reaction and the resulting 1H NMR spectra for both the crude (shown in purple) and purified products (shown in red) are included. As can be seen the spectra for the modified polymer varied substantially from the base polymer and from the mixture of isoprop/PAM-co-AA. The additional peaks present in the spectra have been assigned confirming successful modification of the polymer. For the

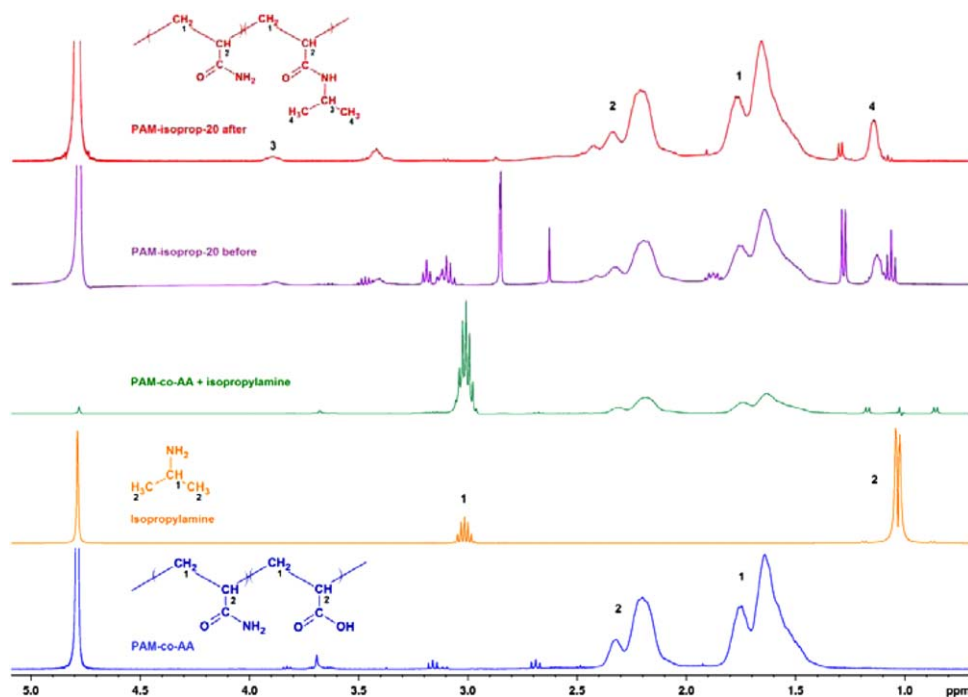


Figure 2. ^1H NMR spectra for the base polymer (shown in blue), isopropylamine (shown in orange) which was used to modify the polymer, a mixture of the isopropylamine and base polymer (shown in green without EDC and NHS), and 20% modified polymer before purification (shown in purple), and 20% modified after purification by re-precipitation into ethanol three times (PAM-isoprop-20, shown in red). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymer before purification the additional peaks are due to the nontoxic isourea and NHS side products (NMR spectra shown in Supporting Information Figure S1). These side products are removed by re-precipitating the polymer three times.

Figure 3 shows ^{13}C NMR spectra for a range of HMWSP and the base polymer. As can be seen the spectra for the base polymer (shown in blue) consists of four major peaks including carbonyl peaks (indicated as C₃ and C₄) and alkyl peaks from the

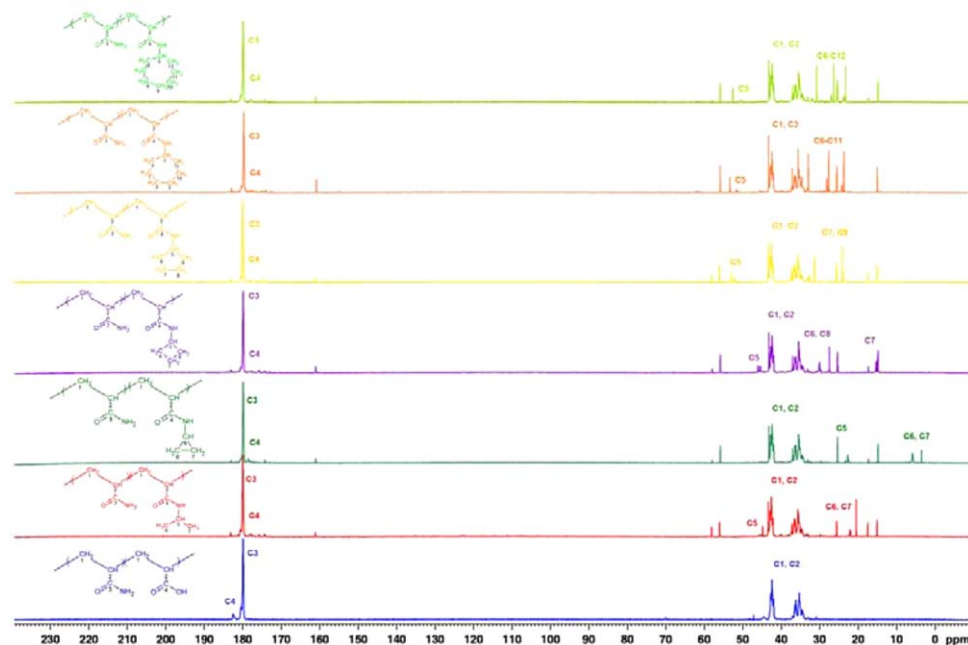


Figure 3. ^{13}C NMR spectra for the base polymer (shown in blue) and 20% modified polymers with different functionality from isopropylamine (PAM-isoprop-20, red), cyclopropylamine (PAM-cycloprop-20, green), cyclobutylamine (PAM-cyclobut-20, purple), cyclopentylamine (PAM-cyclopent-20, yellow), cycloheptylamine (PAM-cyclohept-20, orange) and cyclooctylamine (PAM-cyclooct-20, green), all polymers have been purified by re-precipitation one time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

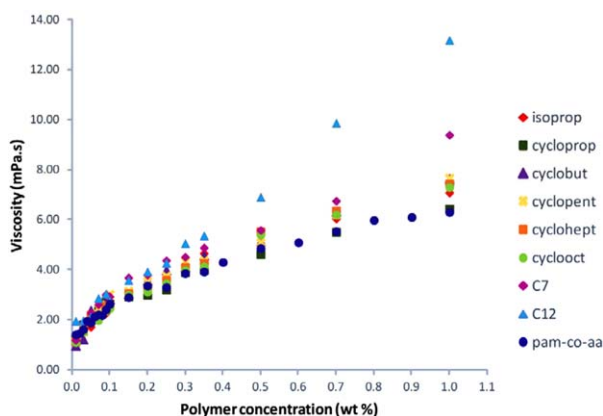


Figure 4. Effect of polymer concentration on the viscosity of a range of modified PAM-based polymers at 25°C with 2 mol % modification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

backbone (C_1 and C_2). For the modified polymers the spectra are different with a number of additional peaks which have been assigned to the functional groups incorporated on the modified polymers.

Viscosity

Synthetic water-soluble polymers have been used for a number of years as viscosity enhancers. The ability to controllably place functional groups is essential to maximizing viscosity. Hydrophobic groups can provide the largest enhancements in viscosity as they tend to associate with each other forming intra or intermolecular aggregates which cause a significant increase in the viscosity of the solution. Figure 4 shows the viscosity for a range of modified-PAMs at different polymer concentrations, each polymer was modified with 2 mol % of functional groups. The primary aim of this study is polymer modification which causes a change in the overall viscosity which demonstrates successful modification. However, optimization of the viscosity is beyond the scope of this study and will be investigated further.

In the hydrolyzed PAM sample used as the base polymer (PAM-co-AA, Figure 4) the modification of the polymer occurs on the AA groups. Before modification these carboxylate groups cause repulsion of the ionic groups resulting in chain extension, thus the viscosity of a solution with HPAM increases.^{30,31} The solubility of the polymers will also increase due to the presence of these charged groups. We replaced 2 mol % of the AA with cycloamine groups or longer alkyl chains. Figure 4 shows the change in viscosity for all of the resulting polymers which demonstrates that the viscosity is sensitive to the structure of the functional group. As can be seen the inclusion of these groups generally increases viscosity compared to the PAM-co-AA base polymer which is due to hydrophobic interactions. As the polymer concentration is increased the viscosity increases for all of the polymers. The functional group that had the largest effect was the long C_{12} alkyl chain (PAM- C_{12} -2) which is attributed to the enhanced hydrophobic interactions because this is the most hydrophobic group included. The effect of polymer concentration on the hydrophobic association, and hence viscosity, is higher due to increased intermolecular associations. There is also a variation in the slope of the

curves for the C_{12} and C_7 polymers that can be linked to a transition in the concentration regime. This variation occurs at lower concentrations for the C_{12} polymer because the intermolecular interactions are facilitated by the greater length of the pendant chains. The C_7 alkyl chain also increased the viscosity whereas the cycloamine groups did not result in a large change in viscosity, this is because these groups are less hydrophobic. The differences in hydrophobicity between the linear and cyclic groups presented here are based on Hansen solubility parameters.³² Linear hydrocarbon chains contribute only dispersion forces (δ_D), which can be enhanced with increasing size of the molecule ($\delta_D = 15.3 \text{ MPa}^{1/2}$ for heptane and $\delta_D = 16.0 \text{ MPa}^{1/2}$ for dodecane), which in turn increases the hydrophobic character of the molecule. Cyclic hydrocarbon chains contribute dispersion forces (δ_D) but also hydrogen bonding (δ_H) ($\delta_D = 16.4 \text{ MPa}^{1/2}$, $\delta_H = 1.8 \text{ MPa}^{1/2}$ for cyclopentane and $\delta_D = 16.8 \text{ MPa}^{1/2}$, $\delta_H = 0.2 \text{ MPa}^{1/2}$ for cyclohexane for example). It is worth noting that the C_7 and C_{12} -modified polymers with 2 mol % modification could also be dissolved quickly because they are terpolymers of acrylamide, AA, and the functionalized groups. Solubility is typically challenging with polymers containing hydrophobic groups. In any case, the viscosity changes do not relate only to the hydrophobic character of the pendant groups, as can be better observed in the results obtained for the series of 20 mol % substitution. A series of polymers were also prepared with increased level of the hydrophobic groups (20 mol %) to observe the effect of functional group concentration. As can be seen for the same functional groups the viscosity of the polymers is very different depending on the concentration (Supporting Information Table S1). This is further evidence of successful modification of the polymers.^{33–36} For HMWSP the maximum concentration that is typically employed is 5 mol %.⁸ However, we modified polymers to 20 mol % to try to react all of the carboxylate groups to generate copolymers containing acrylamide and the functionalized group. The solubility of the resulting polymers in water became challenging as the amount of hydrophobic groups increased. As a result the polymer modified with C_{12} groups at 20 mol % was insoluble in water. This indicates that the reaction was successful as the solubility changed. The polymers that remained soluble had a lower viscosity than the base polymer (PAM-co-AA, Figure 5). This is strong evidence that including >5 mol % of hydrophobic groups can actually have a detrimental effect of enhancement of the viscosity. It also demonstrates that the remaining carboxylate groups in the polymers modified with 2 mol % (Figure 4) are potentially contributing to the enhanced viscosity seen in Figure 4 in comparison to the PAM-co-AA base polymer. Regarding the effect of pendant group structure on the viscosity, the results obtained for this series of 20 mol % substituted groups do not show a direct correlation between the hydrophobicity of the pendant group and viscosity. Once the systems seem to be in a dilute concentration regime and have a high content of pendant groups, there are no intermolecular interactions between the molecules which undergo contraction due to intramolecular hydrophobic interactions. The degree of contraction of the polymer coil is generally associated with the degree of hydrophobicity of the pendant groups. However, it can also be associated with the space for accommodating these groups in the most contracted conformation. Chains containing pendant

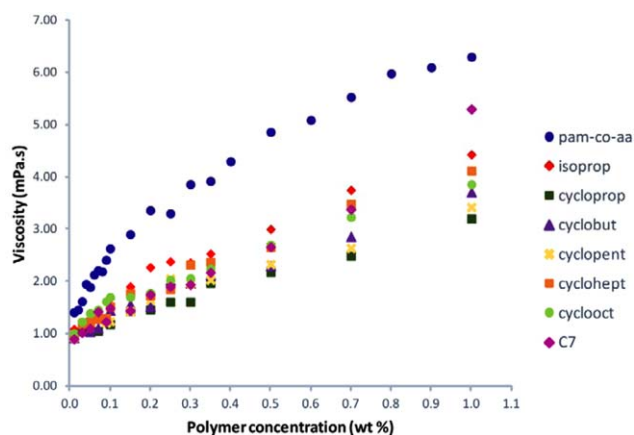


Figure 5. Effect of polymer concentration on the viscosity of a range of modified PAM-based polymers at 25°C with 20 mol % modification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cyclic groups seem to allow greater contraction of the chain than linear C_7 chains than branched isopropyl groups due to the spatial arrangement established.

Rheology

Some polymer solutions show shear thinning under certain conditions which is useful for applications such as drilling fluids where the polymer can suspend cuttings at low shear rate but offer little resistance to flow at high shear rates.² For example, if shear rate is increased the entangled polymer chains unfold resulting in a decrease of viscosity. In addition the higher shear force also reduces the attraction between the polymers chains. However, for polymers that can form micelles the opposite is observed as higher shear rates increase solution viscosity. The PAM- C_{12} -2 (5 wt %) shows a clear shear thinning hydrodynamic behavior (Figure 6) and follows an approximate power law dependence on the shear rate. This suggests that the C_{12}

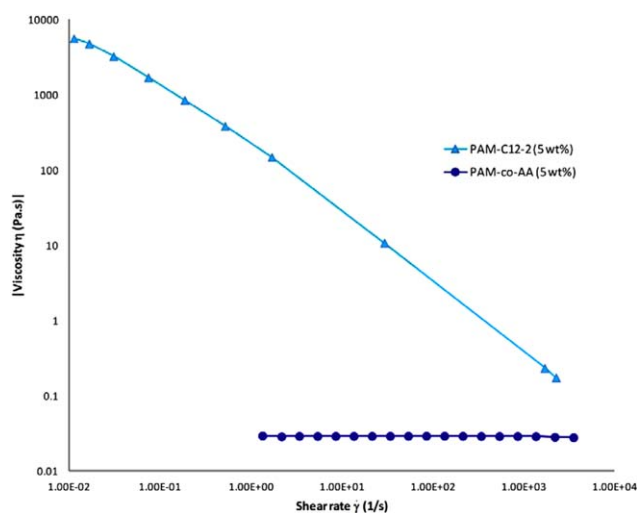


Figure 6. Log-log plot of shear thinning behavior of modified polymer PAM- C_{12} -2 and the base polymer PAM-co-AA, 5 wt % solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

functional groups are well distributed along the polymer chains. In contrast, the base PAM-co-AA polymer (5 wt %) displays shear rate independent viscosity.

Hydrophobically Modified Hydrogel Synthesis

To demonstrate the flexibility of this approach a polymer was modified with 2 mol % of C_{12} groups (PAM- C_{12} -2, Table I) and the remaining carboxylate groups were cross-linked with ethylene diamine, which is a method we introduced recently.²⁴ The reaction was tracked with rheology and a well-developed hydrogel was formed with the storage modulus being higher than the loss modulus (Supporting Information Figure S2). The intersection of both curves cannot be observed in Figure S2 due to the fast reaction so the cross-linking was occurring as the hydrogel precursor solution was added into the rheometer. Hydrophobically modified hydrogels can often display enhanced toughness³⁷ and the gel prepared in this study displays a high storage modulus (>1000Pa).

CONCLUSIONS

Water-soluble synthetic polymers based on acrylamide are versatile materials that are applied in a number of areas. They suffer from a number of limitations including stability which requires the development of new synthetic protocols that can accurately control polymer structure and hence performance. This work demonstrates that functionalized acrylamide-based polymers, including HMWSP, can be generated using a CMC reaction onto an existing PAM-co-AA polymer. This is supported by detailed investigation of the resulting polymers using acid-base titration, NMR spectroscopy, viscosity, and rheology. The reaction converts the AA in the base polymer to target functional groups which results in a decrease in the acid number. NMR spectroscopy provides further confirmation of the structure of the polymers showing that the CMC reaction is an efficient tool for controlling polymer structure. The viscosity of the resulting polymers is dependent on the structure of the functional group, the level of incorporation, polymer concentration, and the degree of hydrolysis. This provides a handle to fine tune the viscosity and polymers with more hydrophobic groups (C_{12}) giving the highest viscosity. Using this method both copolymers (acrylamide and functional groups) and terpolymers (acrylamide, AA, and functional groups) can be readily generated. The reaction proceeds efficiently in water at room temperature using commercially available reagents. A single base polymer was used for the modification so all of the polymers have the same molecular weight. The CMC post-synthetic modification reaction is a flexible method that can be used to fine tune properties such as viscosity or stability for a broad range of applications as well as access hydrogels.

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