

Use of a CO₂-Switchable Hydrophobic Associating Polymer to Enhance Viscosity-Response

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ABSTRACT: A series of copolymers, poly(acrylamide)-*co*-poly(*N,N*-dimethylaminoethyl methacrylate)-*co*-poly(*N*-cetyl DMAEMA) (abbreviation PDAMCn), was synthesized with different monomer ratios. The resulting copolymer solution shows pronounced viscosity-response property which is CO₂-triggered and N₂-enabled. Electrical conductivity experiment shows that tertiary amine group on DMAEMA experiences a protonate and deprotonate transition upon CO₂ addition and its removal. In addition, different incorporation rates of DMAEMA leads to two kinds of morphological change in the presence of CO₂ and thus induces different rheological behaviors. PDAMCn incorporating longer hydrophobic monomer (C₁₈DM) show more pronounced initial viscosity and higher critical stress required to cause network deformation, which consequently enhances the viscosity-response property of the solution. The addition of NaCl could also tune the viscosity of PDAMCn solution. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41468.

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INTRODUCTION

Hydrophobic associating water-soluble polymers (HAWSP) or modified polymers¹ have been extensively studied from the theoretical and experimental points of view on account of their unique rheological characteristics^{2–4} as thickeners, such as in enhanced oil recovery,⁵ drilling fluids.^{6,7} These polymers are tailored on the basis of a hydrophilic structure,⁸ which ensures the overall solubility in water, with a small amount of hydrophobic moieties,^{9,10} that usually by introducing rigid or long species^{11–13} to the side chain, through covalently bound. The general idea to boost the viscosity is through the formation of large intermolecular networks due to the self-association of hydrophobic moieties in the aqueous media. However, the viscosity of these conventional HAWSP can only be tuned by controlling the concentration of polymer and inorganic salts. To the best of our knowledge, there are hardly any reports on smart viscosifiers, the viscosity of which could be accurately adjusted to meet the requirement of diverse formations. In 2012, Yue zhao¹⁴ designed a CO₂-switchable polymer poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA) which could directly react with CO₂ in water with functionalization with tertiary amine. Upon this idea, the hydrophobic associated polymer could acquire a smart viscosity-tuning capacity if the tertiary

amine group that could experience a reversible transition between hydrophobic and hydrophilic state upon CO₂ addition and its removal^{15,16} is introduced in it. Carbon dioxide is a kind of nontoxic, inexpensive, abundant, and an environmentally friendly chemical reagent.¹⁷ Thus, a viscosity-tuning HAWSP triggered with this simpler and environmentally benign stimulus may give a new access to develop controllable viscosity thickener in oil field.

In our previous works, a series of copolymers, PDAMs, were synthesized with different monomer ratio of acrylamide and *N,N*-dimethylaminoethyl methacrylate (DMAEMA).¹⁸ The PDAMs solution shows a special property of viscosity-response which is CO₂-triggered and N₂-enabled. However, performance of PDAMs solution still hardly reaches the requirements of practical applications. Therefore, on the basis of PDAMs, we make a further research. In this article, poly(acrylamide)-*co*-poly(*N,N*-dimethylaminoethyl methacrylate)-*co*-poly(*N*-cetyl DMAEMA) (PDAMCn) were synthesized with a series of monomer ratio of acrylamide, DMAEMA and hydrophobic monomer *N*-cetyl DMAEMA. Long-chain hydrophobic monomer will perhaps endow the copolymer a stronger hydrophobic associating behavior, which consequently affects the switching behavior of viscosity. The corresponding mechanism of

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viscosity variation is also illustrated by zeta potential and dynamic light scattering (DLS).

EXPERIMENTAL

Materials

2-(Dimethylamino)ethyl methacrylate (DMAEMA, 98%) and 2,2'-azobisisobutyronitrile (V-50) were purchased from sigma-Aldrich chemicals and stored at $-10 \pm 0.5^\circ\text{C}$. Acrylamide, acetone, ethanol, bromohexadecane, bromo octadecane (Kelong, $\geq 98\%$), carbon dioxide (Jinli, 99.99%), and nitrogen (Jinli, 99.99%) were used without further purification. All aqueous polymer solutions were prepared using ultrapure water from a Millipore Milli-Q system.

Sample Preparation

Preparation of Hydrophobic Monomer. DMAEMA (8.43 g, 0.054 mol) and bromohexadecane (18 g, 0.047 mol) were added into a flask containing 30 mL acetone. The mixture was sealed and placed in a dark place at $25 \pm 1^\circ\text{C}$, and then the solution was precipitated in iced water after 3 days complete reaction. Then the precipitate was recrystallized three times from acetone and was then dried in a vacuum oven for 12 h at $40 \pm 1^\circ\text{C}$. The product, abbreviation C_{16}DM was recovered as a white powder yielding in 5.04 g. $^1\text{H NMR}$ (400 MHz, D_2O): 0.826 (3H, CH_2-CH_3), 1.233 (24H, CH_2CH_2), 1.876 (3H, $\text{C}-\text{CH}_3$), 3.212 [6H, $\text{N}^+- (\text{CH}_3)_2$], 3.809 (2H, $\text{CH}_2-\text{CH}_2-\text{O}$), 4.614 (2H, $\text{CH}_2-\text{CH}_2-\text{O}$), 5.557, 6.119 (2H, $\text{CH}_2=\text{C}$). Another hydrophobic monomer, C_{18}DM , was synthesized in a similar manner, but bromo octadecane was used as the alkylating agent.

Synthesis of PDAMCn. The random polymer was synthesized by a previously reported method¹⁹ for similar compounds. In this work, PDAMCn were synthesized by different mole ration of DMAEMA, AM, and C_{16}DM . Mol (DMAEMA) : mol (AM) : mol (C_{16}DM) is varied from 1 : 9 : 0.05, 2 : 8 : 0.05, 3 : 7 : 0.05, 4 : 6 : 0.05, 5 : 5 : 0.05, 6 : 4 : 0.05, 7 : 3 : 0.05, 8 : 2 : 0.05, to 9 : 1 : 0.05, and the corresponding copolymer are remarked as PDAMC₁₀, PDAMC₂₀, PDAMC₃₀, PDAMC₄₀, PDAMC₅₀, PDAMC₆₀, PDAMC₇₀, PDAMC₈₀, and PDAMC₉₀, respectively. The copolymer with 30% content of DMAEMA units, for example, was synthesized in aqueous solution. DMAEMA (4.76 g, 0.03 mol) was first added to 40 mL deionized water and was bubbled with CO_2 for 10 minutes. Then, acrylamide (4.999 g, 0.07 mol), C_{16}DM (0.19 g, 0.99 mmol) and V-50 (0.03 g) were added until completely dissolved. After the solution under stirring was purged by CO_2 flow for 5 min, the flask was sealed and the polymerization was carried out under a CO_2 atmosphere at $45 \pm 1^\circ\text{C}$ for about 8 h. Subsequently, the polymerization was terminated and the crude products were then precipitated in a large volume of ethanol. After filtration, the precipitate was washed several times with ethanol and was dried in vacuum environment at $50 \pm 1^\circ\text{C}$ for 24 h. $^1\text{H NMR}$ (400 MHz, D_2O): 1.062 (33H, $-\text{C}_{16}\text{H}_{33}$), 1.582 (2H, 3H, $\text{CH}_2-\text{C}-\text{CH}_3$), 2.138 (1H, $\text{CH}-\text{CONH}_2$), 2.851 (3H, $\text{N}-\text{CH}_3$), 3.099 (2H, $\text{CH}_2-\text{N}-\text{CH}_3$), 3.836 ($\text{O}-\text{CH}_2\text{CH}_2$), 6.174 (2H, NH_2). The polymerization of another HAWSP with C_{18}DM as hydrophobic monomer is carried out under similar conditions.

Measurement of CO_2 -Switchable

Conductivity Measurement. PDAMCn contain tertiary amine groups, which could be protonated by CO_2 to form a hydrophilic ammonium bicarbonate and be deprotonated upon N_2 . Reversible ability of PDAMCn can be monitored by conductivity tests. The conductivity of 2 mg/mL of PDAMCn solutions was determined using a Jenway conductivity meter DDS-11A at $25 \pm 1^\circ\text{C}$. CO_2 was bubbled through the solution using a needle at the flow rate of 300 mL/min (determined using a Varian intelligent Digital Flowmeter) until reaching a constant conductivity value. N_2 was bubbled through the solution at the same rate subsequently. This process was repeated for three cycles.

Zeta-Potential Analysis. Since zeta potential is the potential at the slipping plane of a particle, it reflects the sign of the charge the particle carries. Zeta potential can be used to evaluate the potential stability of the colloidal system. Therefore, to investigate the aggregation and desperate behavior of PDAMCn in aqueous solution, zeta-potential analysis measurements were employed in the cycle of bubbling with CO_2 and N_2 . It was measured on a Brookhaven Instrument Zeta PALS 190 Plus. Zeta-potential measurements were carried out within 24 h after sample solutions were prepared. Samples were loaded in optical cuvettes with 1 cm path length and equilibrated at $25 \pm 1^\circ\text{C}$.

Measurements of Viscosity

Copolymer sample was weighed accurately, swelling in pure water for 4 h, and then being placed on a constant temperature shaker and shaken for 12 h to ensure the copolymer was completely dissolved. Afterward, the solution was diluted and copolymer aqueous solutions with different concentrations were prepared. A series of experiments were measured by Brookfield DV-III rotational viscometer.

Assessing CO_2 -Combination Stability

All PDAMCn solutions were saturated with CO_2 for 30 min bubbling at a speed of 300 mL/min, taking viscosity measurement of the saturated solution at once. Then these solutions were exposed to air for 1 h and the viscosity measurement was performed at every 10 min interval.

Dynamic Light Scattering

Measurements of polymer particle-size were performed at $25 \pm 1^\circ\text{C}$ using a Brookhaven BI-200SM goniometer. Each sample was balanced for 30 s before measurement. The scattered light intensity of each sample was measured for five times.

RESULTS AND DISCUSSION

These new series of associated polymers PDAMCn not only have the feature of unique rheology as a conventional thickener but also have remarkable CO_2 -triggered viscosity-responsive property. Photographs are shown in the Figure 1. The original solutions of PDAMC₁₀, PDAMC₂₀, PDAMC₃₀, and PDAMC₄₀ are colorless and transparent. PDAMC₅₀ and PDAMC₆₀ turn gradually to be white but still lucid, while the solution of PDAMC₇₀, PDAMC₈₀ and PDAMC₉₀ appear a varying degree opaque and milk-white color. When treated with CO_2 , the solution of PDAMC₅₀ and PDAMC₆₀ become deep milk-white, while other groups show no change in their appearance. Followed by bubbling with N_2 , all groups of PDAMCn turned back

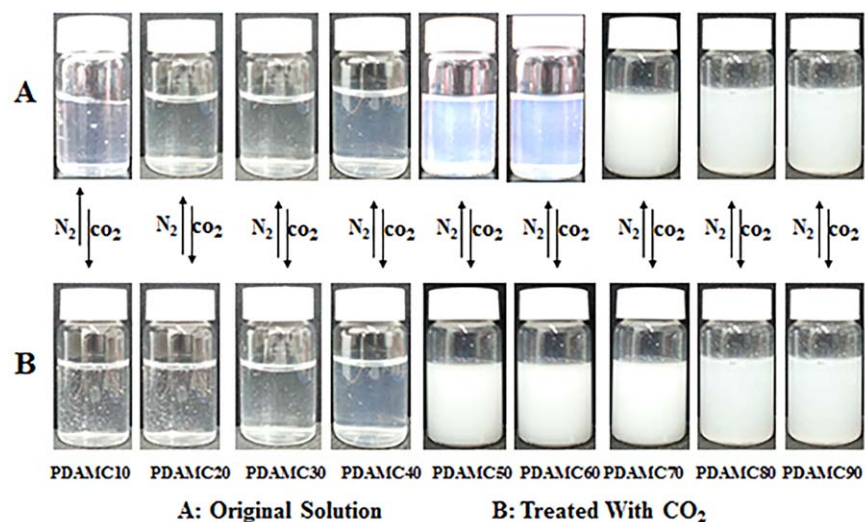


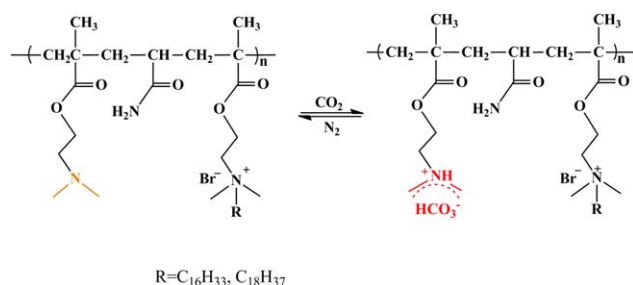
Figure 1. Photographs of the PDAMCn solutions (10 mg mL^{-1}) after bubbling CO_2 and N_2 through the solutions at ambient temperature (25°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to the initial appearance. The conductivity measurement and zeta-potential analysis are applied to testify the switchable ability of PDAMCn. PDAMCn with different molar ratio have been divided into two series. PDAMC₁₀, PDAMC₂₀, PDAMC₃₀, PDAMC₄₀, PDAMC₅₀, and PDAMC₆₀ belong to series A. Series B includes PDAMC₇₀, PDAMC₈₀, and PDAMC₉₀.

CO_2/N_2 Switchable Ability of PDAMCn

It has been demonstrated previously that amidine and tertiary amine switchable surfactants form bicarbonate when reacted with CO_2 .^{20,21} PDAMCn contain tertiary amine groups, which could be protonated by purging CO_2 to form a hydrophilic ammonium bicarbonate (Scheme 1). The reversibility of conversion from uncharged base to bicarbonate salts was demonstrated by bubbling CO_2 followed by nitrogen through the solutions of PDAMCn and measuring the change of conductivity and zeta potential of the solution.

Conductivity Measurements. When CO_2 is passed through the PDAMC₇₀ solution and pure water respectively for 10 min, the conductivity of PDAMC₇₀ solution rises significantly from 109 to $195 \mu\text{S cm}^{-1}$ but the conductivity of pure water does not change (conductivity is always zero), implying that a number of protonated tertiary amine formed on the copolymer chains. The



Scheme 1. Reaction of PDAMCn with CO_2 forming charged bicarbonate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

minimum conductivity reached after 50 min of bubbling with N_2 for PDAMC₇₀ is $138 \mu\text{S cm}^{-1}$. This procedure is repeated for three cycles (Figure 2). The following two cycles present a similar trend and all the other PDAMCn exhibit the same reversible conductivity variation.

Zeta-Potential Analysis. Electrostatically stabilized colloidal dispersions are stabilized by a diffuse electrical double layer that surrounds the surface of the latex.²² The double electrode layer involves two parallel layers of charge which can be reflected accurately by the value of zeta potential. Zeta-potential measurements could also provide the information about the CO_2 -switchable property and potential stability of PDAMCn. It is found in Table I, after bubbling with CO_2 , the absolute values of ζ of series A decrease and it indicates that the polymer tends to aggregate and becomes less stable in aqueous solutions. In contrary, the absolute values of ζ of the B series increase in the presence of CO_2 . With large negative or positive zeta potential, particles tend to repel each other and to disperse in the

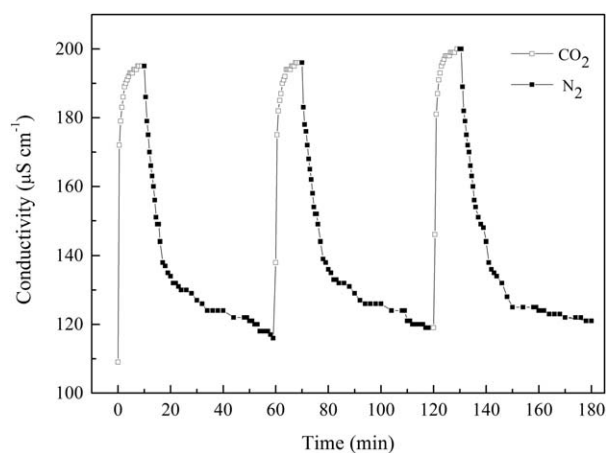


Figure 2. Conductivity changes for the PDAMC₇₀ over three cycles of switching triggered by CO_2 and N_2 .

Table I. Zeta Potential of PDAMC_n (10 mg mL⁻¹) Solutions After Treated with CO₂ and N₂

Sample	Zeta potential		
	Original	After CO ₂	After N ₂
PDAMC ₁₀	-33.41	-25.99	-30.61
PDAMC ₂₀	-29.48	-22.27	-27.92
PDAMC ₃₀	-26.13	-18.52	-25.26
PDAMC ₄₀	-24.09	-16.16	-22.68
PDAMC ₅₀	-22.59	-14.72	-21.05
PDAMC ₆₀	-21.87	-13.11	-20.19
PDAMC ₇₀	-20.87	28.39	-18.64
PDAMC ₈₀	-18.66	24.34	-13.75
PDAMC ₉₀	-17.25	20.07	-11.23

All solutions were subjected to 20 min of CO₂ and 40 min of N₂ bubbling at a flow rate of 300 mL min⁻¹.

system.²³ Thus, the polymer presents a tendency to disperse and becomes more stable in aqueous solutions. When treating with N₂, the absolute value of ζ of all solutions restored closely to the initial value.

Conductivity and Zeta potential confirms that PDAMC_n have CO₂/N₂ switchable ability. But the value of conductivity or zeta potential of PDAMC_n cannot entirely restore the initial value even bubbled with adequate N₂. Quantitative analysis on how much N₂ is required to remove the CO₂ is carried out on the basis of the pH change of saturated carbonated water when sparged with N₂ to remove the dissolved CO₂ (Figure 3). The pH increases from 3.98 (CO₂ saturated water) to 6.69 (close to pure water 7.08) when N₂ is bubbled through the CO₂ saturated water for 40 min. It can be rough calculated from concentration of H⁺ that 99% of dissolved CO₂ could be removed when N₂ is four times amount of CO₂ in the solution. The conductivity thereby could be but not completely recovered by nitrogen.

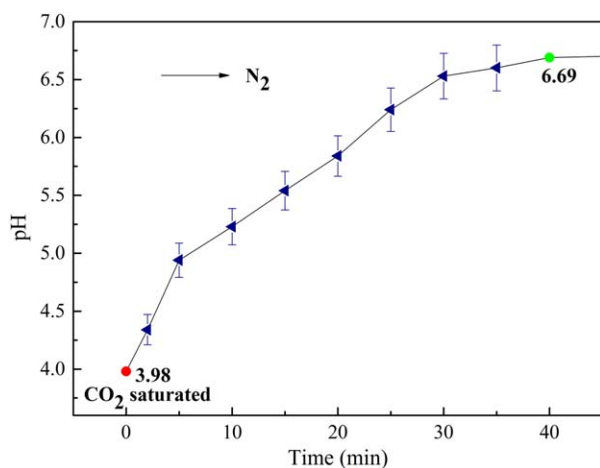


Figure 3. Effect of sparging time on the pH of CO₂ saturated solution when sparged with N₂ (pH is determined by PHSJ-5 pH meter). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CO₂-Triggered Viscosity-Response

Hydrophobic tertiary amine groups can be protonated and transformed into soluble bicarbonate salt by reacting with CO₂, the charged amine groups cause an increased electrostatic repulsion among PDAMC_n molecule chains, which lead to molecular microstructure change and, consequently, result in two different variations of their viscosity: a significant viscosity-decrease is observed for series A by reacting with CO₂, while series B displayed an increased quantify. The viscosity of both series A and series B could almost recover to the initial value by passing through N₂.

Switching Decrease of Viscosity. In series A, the viscosities of PDAMC_n decrease significantly by reacting with CO₂ and then increase upon N₂ addition [Figure 4(a)]. Due to the influence of long-chain hydrophobic monomer (C₁₆DM), PDAMC_n molecules could establish an intermolecular hydrophobic associated structure in original aqueous solutions. Bubbling CO₂ through the original solutions can protonate the amine groups of

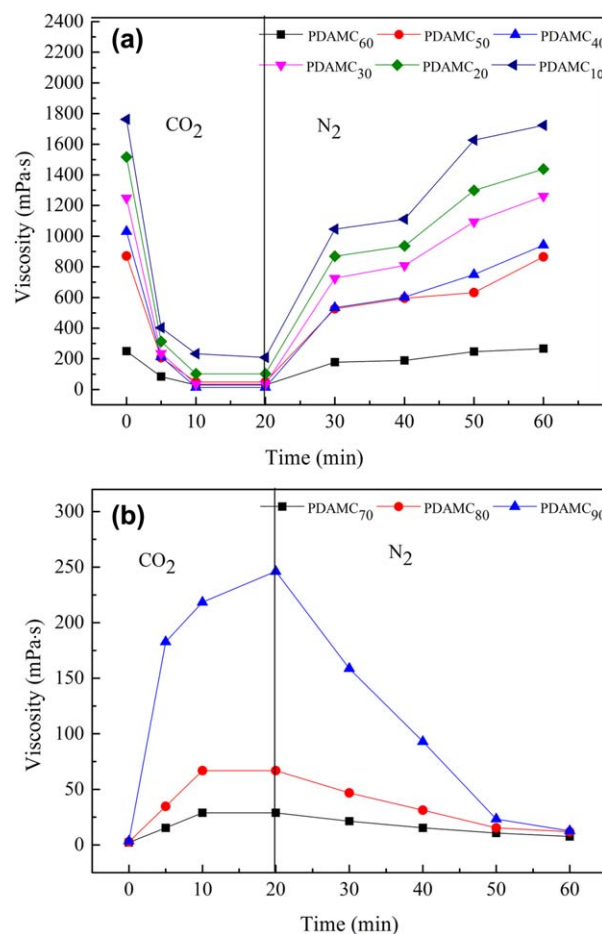
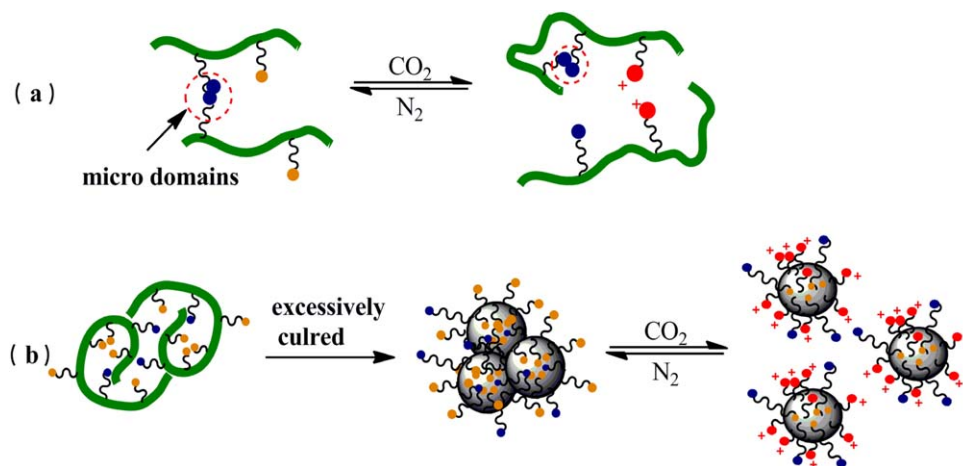


Figure 4. (a) The aqueous solutions contain PDAMC_n, 10 mg mL⁻¹ in series A (PDAMC₁₀, PDAMC₂₀, PDAMC₃₀, PDAMC₄₀, PDAMC₅₀, and PDAMC₆₀). The solutions were switched between high and low viscosity states by alternating CO₂ and N₂ at 25°C. (b) The aqueous solutions contain PDAMC_n, 10 mg mL⁻¹ in series B (PDAMC₇₀, PDAMC₈₀, and PDAMC₉₀). The solutions were switched between low and high viscosity states by alternating CO₂ and N₂ at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Scheme 2. (a) Morphological change of PDAMCn (DMAEMA mol % $\leq 60\%$) in aqueous solution when treated with CO_2 and intuitively explains the mechanism of its viscosity-decrement. (b) Morphological change of PDAMCn (DMAEMA mol % $> 60\%$) in aqueous solution when treated with CO_2 and intuitively explains the mechanism of its viscosity-increment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PDAMCn side chains and form charged hydrophilic bicarbonate. Hence intermolecular electrostatic repulsions gradually increase by bubbling CO_2 . The electrostatic repulsions are gradually dominant rather than the intermolecular hydrophobic interactions, and thus lead to disruption of intermolecular associations and formation of intramolecular interactions (Scheme 2). The significant decrease in the solution viscosity of series A is attributed to this effect. DLS experiment shows that, take PDAMC₅₀ as an example (Figure 5), the diameter of PDAMC₅₀ decreases from 2808nm to 1320nm when treated with CO_2 . This suggests that the significant viscosity-loss of series A is due to the transformation of intermolecular from intramolecular associations.

Switching Increase of Viscosity. In series B, the viscosity of PDAMC₇₀, PDAMC₈₀, and PDAMC₉₀ display a sharp increase of their viscosity by bubbling CO_2 through the original solution and then the viscosity decreased closely to the initial value followed by treatment with N_2 . The result is illustrated in Figure 4(b). The presence of large volumes of hydrophobic groups on

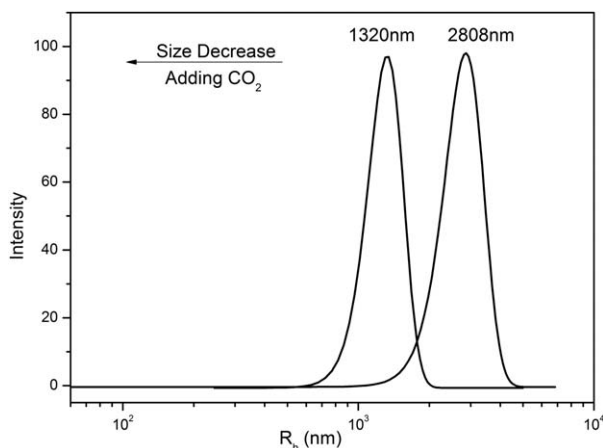


Figure 5. DLS data for PDAMC₅₀ in the absence of CO_2 and in the presence of CO_2 .

the polymer backbone leads the polymer to form a much more compact structure, which is called a hypercoil.²⁴ In original solutions, large volume of hydrophobic DMAEMA on polymer chain causes the polymer chains excessively curled or even construct a small spherical cluster (Scheme 2). Part of hydrophobic groups, including DMAEMA and long-chain groups, is embedded in polymer chains which result in the shielding of intermolecular interactions and consequently the low viscosity of the original solution. In addition, CO_2 would rather contact with limited bared tertiary amines on the surface of the spherical clusters than embedded amine groups. At this point, combined CO_2 could be easy to be removed. Therefore, when exposed to air, the viscosity of CO_2 -treated solutions of PDAMC₇₀, PDAMC₈₀, and PDAMC₉₀ decrease rapidly and significantly (Table II). The PDAMC₇₀, PDAMC₈₀, and PDAMC₉₀ solutions experience a worse CO_2 -combination stability than others. By the reaction with CO_2 , tertiary amine groups of polymer molecule side chains were protonated and resulted in an increment of surface charge, which is consistent with the increment of zeta-potential. What's more DLS experiment shows that, take PDAMC₇₀ as an example (Figure 6), the diameter of PDAMC₇₀ increases from 553.2nm to 1206.9nm when treated with CO_2 . The high degree of ionization (by CO_2) leads to chain extension and further results in a viscosity increment of PDAMCn. When CO_2 is removed by introducing N_2 , the charged bicarbonate is deprotonated and the viscosity of PDAMCn is recovered.

Enhanced Switching Behavior of Viscosity by Hydrophobic Association of PDAMCn

In our previous works, A series of copolymers PDAMs were synthesized with varying monomer ratio of AM and DMAEMA. It has been demonstrated that PDAMs in aqueous solution could form an associated structure due to hydrophobic amine group in DMAEAM. The terpolymer PDAMCn incorporating the C₁₆DM hydrophobe processes a stronger hydrophobic association than PDAMs. The Figure 7 shows that the viscosity of PDAMCn is much higher than the viscosity of PDAMs when the concentration is approximately over 5000 ppm: a strong

Table II. Viscosity of All PDAMC_n Aqueous Solutions (10.0 mg mL⁻¹) After CO₂ Bubbling Through the Solutions for 30 min First and then Exposure into Air

Time (min)	Viscosity (mPa s)				
	PDAMC ₁₀	PDAMC ₂₀	PDAMC ₃₀	PDAMC ₄₀	PDAMC ₅₀
0	1038.5	783.6	464.2	279.4	128.6
10	1050.4	787.9	470.2	297.8	223.4
20	1060.1	796	480.7	322	307
40	1064.5	804.9	495.1	340.8	398.6
60	1070.4	819.1	509.5	370.7	469.4

Time (min)	Viscosity (mPa s)			
	PDAMC ₆₀	PDAMC ₇₀	PDAMC ₈₀	PDAMC ₉₀
0	29.8	406.7	238.5	75.4
10	88.6	212.4	131.6	51.9
20	152.3	149.3	91.8	34.8
40	197.8	91.4	61.3	30.8
60	221.8	67.3	44.9	27.8

The viscosity measurement was processed per 10 min.

associative behavior is thus clearly evidenced. It can be concluded that the PDAMC_n enhances the association and a polymeric network is formed in the solution when the concentration exceeds the CAC. Furthermore, PDAMC_n have a larger effective diameter than PDAMs. (Supporting Information Table S1: PDAM₇₀ 797.8 nm, PDAMC₇₀ 1203.1 nm). Once the associating network was destroyed, viscosity-variation of PDAMC_n is more obvious than PDAMs. Therefore, PDAMC_n have more pronounced viscosity-response property than PDAMs.

Though PDAMC_n have two different viscosity responding behaviors, the variation of viscosity is more obvious than PDAMs when treated with CO₂ and followed by N₂ (Table III). It has been proved from our previous works that PDAMs with

low concentration of DMAEMA (<30%) experience a viscosity reduction owing to a transformation from intermolecular association to intramolecular association by bubbling with CO₂. PDAMC_n with low concentration of DMAEMA (<70%) have stronger intermolecular hydrophobic associated structure. Once the intermolecular association was broken by CO₂, the destruction of the association in PDAMC_n solution is more obvious than it in PDAMs solution. Therefore, the viscosity-loss of PDAMC_n is more apparent, and even inevitable, than corresponding PDAMs. The viscosity of PDAMC_n was influenced by two effects under the atmosphere of CO₂ when improving the concentration of DMAEMA. Firstly, the curled polymer chain was stretched due to polyelectrolyte effect, which is coincident

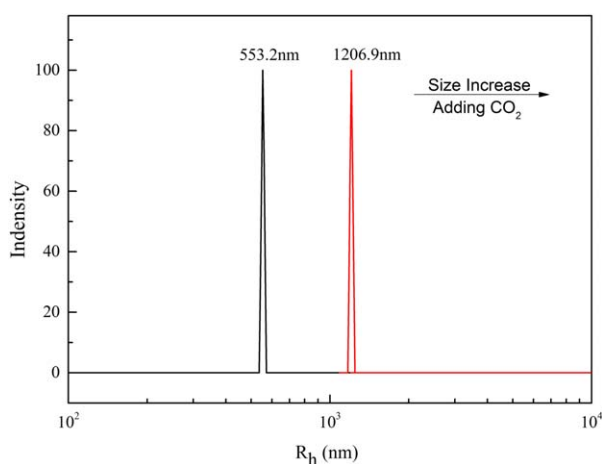


Figure 6. DLS data for PDAMC₇₀ in the absence of CO₂ and in the presence of CO₂. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

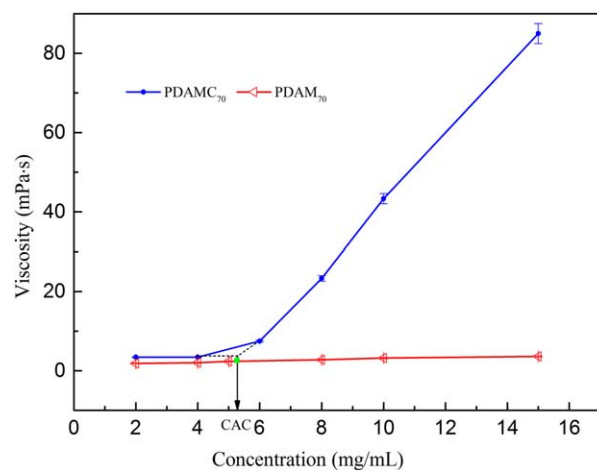


Figure 7. Variation of apparent viscosity with the relative concentration of PDAMC₇₀ and PDAM₇₀. Experiments were performed at 7.34 s⁻¹. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Viscosity Variation of PDAMC_n and PDAMs with Different Mole Ratio at 25°C in Response to CO₂

PDAMC _n	Viscosity (mPa s)			PDAMs	Viscosity (mPa s)		
	Original	After CO ₂	After N ₂		Original	After CO ₂	After N ₂
PDAMC ₁₀	6360.3	1038.5	5213.6	PDAM ₁₀	141.68	77.28	124.75
PDAMC ₂₀	4782.6	783.6	3838.1	PDAM ₂₀	240.63	103.88	227.47
PDAMC ₃₀	3526.1	464.2	2782.7	PDAM ₃₀	393.78	5.67	199.58
PDAMC ₄₀	2707.5	279.4	2076.3	PDAM ₄₀	2.1	47.24	1.68
PDAMC ₅₀	2164.2	128.6	1573.4	PDAM ₅₀	1.6	9.81	2.67
PDAMC ₆₀	1257.9	29.8	982.4	PDAM ₆₀	2.5	7.5	3.87
PDAMC ₇₀	43.3	406.7	19.3	PDAM ₇₀	3.2	9.59	5.23
PDAMC ₈₀	31.4	238.5	12.6				
PDAMC ₉₀	22.3	75.4	8.2				

with the variation of PDAMs. What's more, long hydrophobic monomers could rebuild a polymeric network in solution after bubbling with CO₂, which makes the PDAMC_n get a better rheology property and enhanced capacity of controlling viscosity.

The experiment is repeated several times to confirm switchable behavior of viscosity. According to Figure 8, each cycle is similar to the CO₂/N₂ stimulation referred to above. Repeated cycles result in a trivial decrease because of a little expelled PDAMC_n.

Effect of Hydrophobe Length on Solution Viscosity. The length of hydrophobe affects the rheological properties of the polymer. Steady shear viscosities (η) as a function of the shear stresses are given in Figure 9 for the PDAMC_n incorporating the C₁₆DM and C₁₈DM hydrophobic monomer respectively at a concentration of 15 mg/mL. At this concentration, the polymers are well above their overlap concentrations and exist in high networked states. As a result, the shapes of two curves are quite similar, although response values differ by decades. PDAMC_n incorporating the C₁₈DM exhibits a more pronounced initial viscosity and higher critical yield stress than PDAMC_n incorporating C₁₆DM. At low shear stresses, a small shear-thickening regime is observed. A plateau region where the viscosity remains

relatively constant with increasing shear stress follows at intermediate shear stresses. At higher shear stresses, the samples become shearing thinning and exhibit decreases in viscosity characterized by two different slopes, C₁₈DM being more significant than the C₁₆DM. Tirtaatmadia et al.²⁵ have observed that hydrophobically modified alkali swellable emulsion (HASE) ATs exhibits similar shear stress profiles and have attributed the initial abrupt change to the deformation of the polymer network. The hydrophobicity of groups can be increased by increasing the length of the groups, which further enhance the associative behavior. It can be concluded that PDAMC_n incorporating longer hydrophobic monomer shows the more pronounced initial viscosity and higher critical stress required to disrupt the network.

Viscosity Depending on Concentration of NaCl. The concentration of inorganic salt in associative polymers solutions has strong influence on the polyelectrolyte conformation and interaction and, consequently, the viscosity. Figure 10 shows that without CO₂, increasing concentration of NaCl causes decreasing viscosity of PDAMC₅₀. Su et al.²⁶ have reported a four-armed hydrophobic associative polymer (PAM₆₀-PDEAEMA₂₀)₄

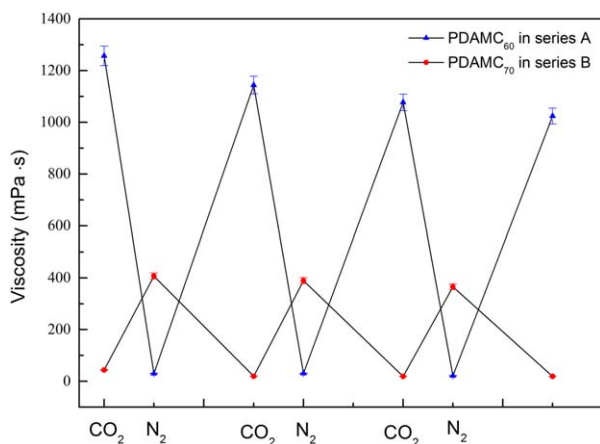


Figure 8. Reversible viscosity change of PDAMC₆₀ in series A and PDAMC₇₀ in series B with rotation speed of 7.34 s⁻¹ upon three cycles of CO₂ (20 min) and N₂ (40 min) bubbling at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

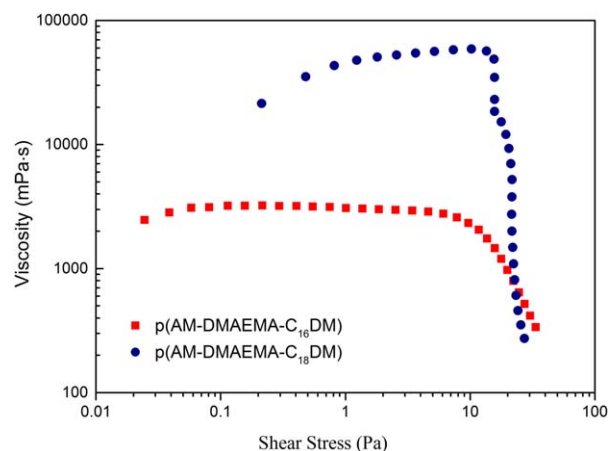


Figure 9. Steady shear viscosities (η) as a function of shear stress for PDAMC_n incorporating C₁₆DM and C₁₈DAM at a concentration of 15 mg/mL. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

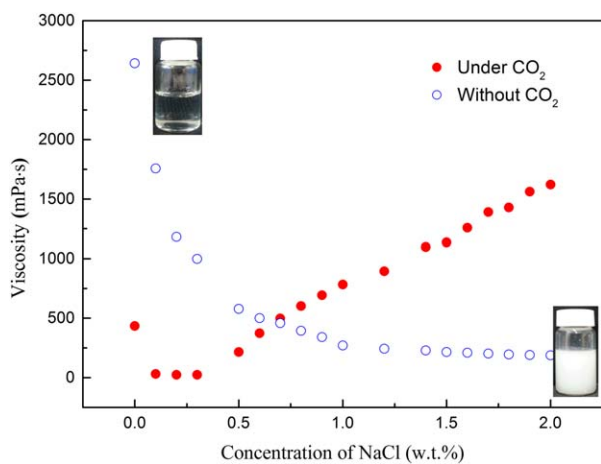


Figure 10. The concentration of NaCl versus the viscosity of the aqueous solution of polymer PDAMC₅₀, 1.5 wt %. Rotation speed is 7.34 s⁻¹ and the temperature is 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that yields aqueous solutions of switchable viscosity, responding to both CO₂ and NaCl as stimuli. In compared with (PAM₆₀-PDEAEMA₂₀)₄, DMAEMA and C₁₆DM on PDAMCn polymer chains both are hydrophobes in the absence of CO₂. On the one hand, the presence of salt causes a shielding of the electrostatic repulsion of C₁₆DM segments and further results in a collapse of the network with loss of the solution viscosity. On the other hand, the solubility of the hydrophobic groups, including DMAEMA and C₁₆, decreases with increasing salt concentration and thus induces precipitation from solution. However, (PAM₆₀-PDEAEMA₂₀)₄ is a neutral associative polymer in the absence of CO₂. The hydrophobic effect tends to be dominant rather than Coulombic forces at high salt concentration, so that the viscosity increases more rapidly at high NaCl concentration. Therefore, without CO₂, the viscosity of PDAMC₅₀ decreases at high NaCl concentration, while (PAM₆₀-PDEAEMA₂₀)₄ exhibits increasing viscosity.

Under a CO₂ atmosphere, the viscosity against salinity curve of PDAMC₅₀ displays a minimum at intermediate concentration of NaCl. For one thing, the originally hydrophobic tertiary amine group on DMAEMA was converted into hydrophilic group by passing through CO₂. The presence of salt screens the electrostatic repulsion thus suppressing the disruption of intermolecular associations by the charged groups. What's more, for the hydrophobic segments (C₁₆), addition of salt can increase the viscosity of the solution because of salting out effect as before. The effect of salt on PDAMCn solution under CO₂ thereby displays a peculiarly aforementioned behavior because of a balance between hydrophobic and electrostatic interaction. At low concentration of salt, intramolecular hydrophobic associations are still dominant and thus result in a decrement of solution viscosity. After knee point, intermolecular hydrophobic associations start to dominate rather than intramolecular associations and thus lead to an increment of the solution viscosity with increasing salt concentration. For (PAM₆₀-PDEAEMA₂₀)₄, increasing concentration of NaCl causes decreasing viscosity. (PAM₆₀-PDEAEMA₂₀)₄ is entirely hydrophilic polymer in the presence

of CO₂. Addition of NaCl decreases the viscosity because Coulombic forces are screened by the brine solution.

CONCLUSIONS

We report the rational design, synthesis, and study of a series of hydrophobic associative polymer PDAMCn that yield pronounced viscosity–response, responding to CO₂. When the incorporation rate of DMAEMA is equal or lower than 60 mol %, a number of charged ammonium groups by treating with CO₂ lead to the disruption of the intermolecular hydrophobic association and consequently induce a significant decrease in the solution viscosity. In contrast, when the incorporation rate of DMAEMA is more than 70 mol %, a more extended conformation is established due to the enhanced repulsive interactions and results in an increment of the solution viscosity. When compared with PDAMs, hydrophobicity of PDAMCn incorporating the C₁₆DM or C₁₈DM hydrophobic monomer increases and a strong associative behavior has been found when the concentration of PDAMCn exceeds the CAC. In addition, PDAMCn incorporating the C₁₈DM hydrophobic monomer show more pronounced initial viscosity and higher critical stress required to cause network deformation. Addition of NaCl reduces the viscosity when CO₂ is absence. When bubbling CO₂, viscosity of PDAMCn solution displays a minimum at intermediate concentration of NaCl.

PDAMCn could be used as a novel efficient viscosity-controlled thickener for enhanced oil recovery. PDAMCn enable operate in cycling and automatically increasing or decreasing its solution viscosity to the designed value by a low cost and environmentally friendly stimulus. Thus it could pave a new access to create the smart thicker in oil field.

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