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A Water-Soluble CO_2-Triggered Viscosity-Responsive Copolymer of *N*,*N*-Dimethylaminoethyl Methacrylate and Acrylamide

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ABSTRACT: A series of copolymers PDAMs were synthesized with varying monomer ratio of acrylamide (AM) and *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA). The resulting copolymer solution shows an interesting property of viscosity-response which is CO_2-triggered and N_2-enabled. Tertiary amine groups of PDAMs experience a reversible transition between hydrophobic and hydrophilic state upon CO_2 addition and its removal, which induced different rheological behavior. A combination of zeta-potential, laser particle-size analysis, and electrical conductivity analysis indicated that, when the monomer mole ratio of DMAEMA and AM is less than or equal to 3 : 7, the hydrophobic association structure between the copolymer molecules was destroyed by the leading of CO_2 and caused a viscosity decrease in its solution. On the contrary, when the monomer mole ratio of DMAEMA and AM is more than 3 : 7, a more extended conformation due to the protonated tertiary amine groups is formed and the enhanced repulsive interactions among the copolymer molecule results in a rise of its solution viscosity. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40872.

KEYWORDS: copolymers; functionalization of polymers; hydrophilic polymers; polyelectrolytes; recycling

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INTRODUCTION

Stimuli-responsive polymers have achieved great attention because of their unique properties. Particularly, CO_2-responsive polymers use CO_2 as a green trigger[1] underwent a rapid development in recent years. CO_2-triggered smart materials including solute, solvent and surfactant were first investigated by Jessop's group[2–4] and then a series of CO_2/N_2 switchable polymer latexes[5–7] were reported. Most of the CO_2-responsive polymers were synthesized by employing an amidine-containing monomer which can react with CO_2 to form charged amidinium bicarbonate and be recovered upon CO_2 removal.[8–10] However, CO_2-responsive compounds based on amidine groups usually require a demanding synthesis, so finding an easy way to synthesis CO_2-responsive compounds would be more helpful for the development of CO_2-responsive polymers. Since 2011, a more general, robust, and efficient approach to synthesis CO_2-responsive polymers has been found. The amine-containing monomer DMAEMA and its analogs were first applied by Zhao and coworkers[11,12] to synthesize a series of linear and block CO_2 switchable copolymers. Pinaud et al.[7] designed readily coagulated and redispersed polymer latexes composed of 2-(diethyl) aminoethyl methacrylate and styrene. The thermal CO_2-responsive monomer DMAEMA with its benefits of easy copolymerized with many types of non-CO_2-responsive monomers have attracted rapidly growing interest and it was used in various applications such as controlled release, gene delivery.[13–16]

In the oil industry, water-soluble thickening polymers were widely used in the process of acidification and fracturing stimulation for enhanced oil recovery.[17] Specially, viscosity-controlled acid such as viscoelastic surfactant-based clean acidizing fluid exhibits excellent shearing resistance property, sand carrying capacity and breaking ability.[18–20] Unfortunately, the acidizing and fracturing flow-back fluids would destroy the environment and its treatment demands huge in cost. Therefore, developing a green and inexpensive water-soluble thickening polymer with viscosity-response is meaningful. Recently, some CO_2/N_2 switchable polymers exhibited viscosity-response properties were reported. Weiss and coworkers investigated the polyallylamine solutions, when treated with CO_2 the formation of carbonate and ammonium centers might "cross-link" polyallylamine (PAA) chains through interchain ionpaired centers and undergoes a rheological behavior switches from solution-type to gel-type conversion process, it was used in the art conservation.[21–23] Nagai et al. detected a reversible chain association/

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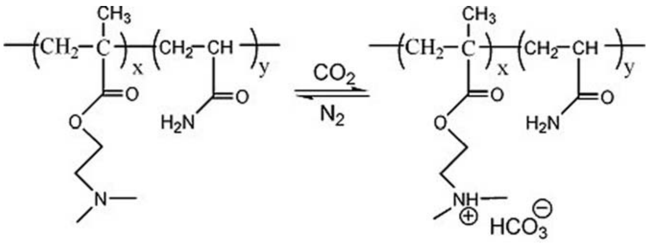


Scheme 1. Reaction of PDAMs with CO$_2$ to form amidinium bicarbonates.

dissociation phenomenon in aqueous PAA; they synthesized a hydrogels composed of polyallylamine and used carbon dioxide as gellant for the development of reversible CO$_2$ absorbent.[24,25] However, to the best of our knowledge, water-soluble CO$_2$-triggered viscosity-controlled polymers combined with amine-containing groups still have been few reports to date.

Herein, PDAMs were synthesized with varying monomer ratio of acrylamide (AM) and *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA) in this study. The resulting copolymer solution shows a viscosity-response property which is CO$_2$-triggered and N$_2$-enabled. The corresponding mechanism of viscosity variation is also researched by zeta-potential, laser particle-size analysis, and electrical conductivity analysis.

EXPERIMENTAL

Materials

AM, acetone, ammonium persulfate, sodium bisulfite (Kelong, ≥98.0%), 2-(dimethylamino) ethyl methacrylate (Aldrich, 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.

Polymer Synthesis and Characterization

Synthesis of PDAMs. PDAMs were synthesized by different mole ratio of DMAEMA and AM. Mol (DMAEMA):mol (AM) is varying from 1 : 9, 2 : 8, 3 : 7, 4 : 6, 5 : 5, 6 : 4, to 7 : 3, and the corresponding copolymer are remarked as PDMA$_{10}$, PDMA$_{20}$, PDMA$_{30}$, PDMA$_{40}$, PDMA$_{50}$, PDMA$_{60}$, PDMA$_{70}$, respectively. DMAEMA was first added to distilled water and was sparged with CO$_2$ for 10 min at the flow rate of 300 mL min^{-1}. Then, AM was added and followed by ammonium persulfate and sodium bisulfite. After the solution under stirring was purged by CO$_2$ flow for 5 min, the flask was sealed and the polymerization carried out under a CO$_2$ atmosphere at 40°C for 8 h. At the end of the reaction, the copolymer was purified by three times of precipitation from acetone, and then it was collected and dried under dynamic vacuum overnight until constant weight.

Characterization. ^{1}H-NMR spectra were recorded on a Bruker Ascend 400 spectrometer (400 MHz) on samples in D$_2$O at room temperature. The amine group was partly protonated in the course of synthetic PDAMs.

PDAMs: ^{1}H-NMR (400 MHz, D$_2$O): 1.013 (3H, C-CH$_3$), 1.649 (2H, C-CH$_2$-C), 1.849 (2H, CH$_2$-C-CH$_3$), 2.872 (3H, N-CH$_3$), 3.219 (2H, CH$_2$-N-CH$_3$), 3.791 (2H, CH$_2$-NH$^+$CH$_3$), 4.315 (2H, O-CH$_2$C), 5.911 (–NH$_2$).

Molecular Weights Measurements

The number–average molecular weight and the weight–average molecular weight of copolymer PDAMs were measured by using Waters e2695 Separations Module. The polymer was dissolved into distilled water forming the solution with concentration of 2 mg mL^{-1}. The measurement was performed at the room temperature (23°C) for 90 min.

Thermo-Sensitive Property Measurements

Hydrophilic thermo-sensitive materials displays a reversible solubility in water in the cycle of heating and cooling.[26,27] The monomer DMAEMA can react directly with CO$_2$ in water and increase drastically its lower critical solution temperature (LCST), characterizing the transition from a soluble to an insoluble state.[28] The PDAMs, which composed of the thermal monomer DMAEMA, could undergo a LCST shift in their aqueous solution when treated with CO$_2$. To test the thermo-sensitive characteristics of PDAMs, transmittance measurements of their original aqueous solutions were employed. Transmittance data of PDAMs aqueous solutions (10 mg mL^{-1}) at different temperatures (20, 30, 40, 50, 60, 70, and 80°C) were determined by type 721-100 visible spectrophotometer.

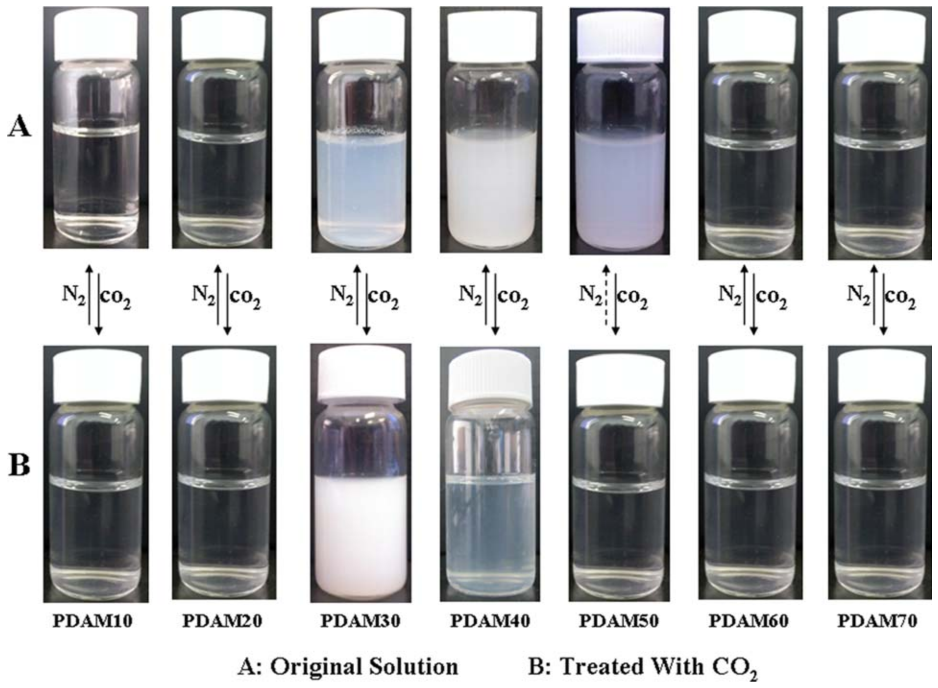
CO$_2$/N$_2$ Switchable Ability Measurements

Conductivity Measurements. The tertiary amine groups in PDAMs could be protonated by the reaction of CO$_2$ and deprotonated upon N$_2$ addition (Scheme 1). The conductivity measurement was carried out to testify this possible reversible protonated and deprotonated course. The conductivity of PDAMs aqueous solutions (10 mg mL^{-1}) was measured using a DDS-11A conductivity meter. CO$_2$ gas bubbled through the solution at room temperature (20°C) for 20 min and after with nitrogen was bubbled for 30 min at a fixed flow rate of 300 mL min^{-1}. The time was measured with an accuracy of 30 s and the carbon dioxide and nitrogen treatment was performed three cycles.

Particle Size and Zeta-Potential Measurements. Zeta potential and laser particle-size analysis measurements are used as an efficient way to detect the molecular morphological changes of polyelectrolyte or surfactant molecules.[29,30] Therefore, in order to investigate the molecule existing form of PDAMs in aqueous solution and its molecular micro-structure variation during the cycle of treatment with CO$_2$ followed by N$_2$, zeta potential and laser particle-size analysis measurements were employed. Particle size and zeta potential data of PDAMs aqueous solutions (10 mg mL^{-1}) was determined by Zeta PALS/90plus.

Viscosities of PDAMs Solutions

A series of experiments were conducted to explore the CO$_2$/N$_2$ switchable viscosity-response properties of PDAMs. Due to the thermal sensitivity properties of monomer DMAEMA, the viscosity characteristics of the original PDAMs solutions and their viscosity-response variations in the cycle of bubbling with CO$_2$ and N$_2$ at different concentration and temperature were investigated. The viscosity was measured by Brookfield DV-III rotational viscometer at 7.34 s^{-1}. All aqueous solutions were



Scheme 2. Photographs of the PDAMs solutions (10 mg mL^{-1}) at 20°C after passing CO_2 and N_2 through the solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

subjected to 20 min of CO_2 and after with nitrogen were bubbled for 30 min at a flow rate of 300 mL min^{-1}.

RESULTS AND DISCUSSION

CO_2/N_2 Switchable Performance of PDAMs

A series of copolymers composed of amine-functionalized monomer DMAEMA and the non-CO_2-responsive monomer AM with different monomer ratio have been prepared in this study. In the cycle of bubbling with CO_2 and N_2, PDAMs solutions present different behaviors. Photographs are shown in the Scheme 2, the original solution of $PDAM_{10}$, $PDAM_{20}$, $PDAM_{60}$, and $PDAM_{70}$ presented colorless and transparency while the solution of $PDAM_{30}$, $PDAM_{40}$, and $PDAM_{50}$ appears a varying degree milk-white color. When treated with CO_2, the solution of $PDAM_{30}$ turns deep milk-white and the solution of $PDAM_{40}$ and $PDAM_{50}$ becomes transparent while the other groups showed no change with its appearance. By bubbling with N_2, all groups of PDAMs turn back to the initial except $PDAM_{50}$, which keeps transparent after the first treat with CO_2. The following conductivity, zeta potential and laser particle-size analysis are applied to testify the switchable performance of PDAMs.

Conductivity. The conductivity of a $PDAM_{10}$ solution at 20°C is shown in Figure 1, the conductivity sharply rise to a maximum value close to 341 μs cm^{-1} when CO_2 was bubbled through the solution, which indicates the tertiary amine is protonated. The conductivity slowly drops to a minimum value close to the original conductivity by the reaction with N_2, which means the protonated tertiary amine restores to the initial. The following two cycles present a similar phenomenon and all the other samples of PDAMs exhibit the same conductivity variation.

Zeta Potential and Laser Particle-Size Analysis. Zeta potential and laser particle-size analysis data of PDAMs in the cycle of bubbling with CO_2 and N_2 are given in Table I. By bubbling with CO_2, the absolute value of zeta potential and the effective diameter of $PDAM_{10}$, $PDAM_{20}$, and $PDAM_{30}$ reduced first and then increase nearly to the initial by the reaction with N_2. On the contrary, the absolute value of zeta potential and the effective diameter of $PDAM_{40}$, $PDAM_{50}$, $PDAM_{60}$, and $PDAM_{70}$ enhance first and then decrease when treated with CO_2 and N_2, respectively. When bubbled with CO_2, the tertiary amine groups of PDAMs are protonated. The different thing is, the intermolecular hydrophobic aggregation of $PDAM_{10}$, $PDAM_{20}$, and $PDAM_{30}$ with low concentration of DMAEMA is broken into intramolecular association, and the particle-size decreased. However, a more extended conformation due to the protonated tertiary amine

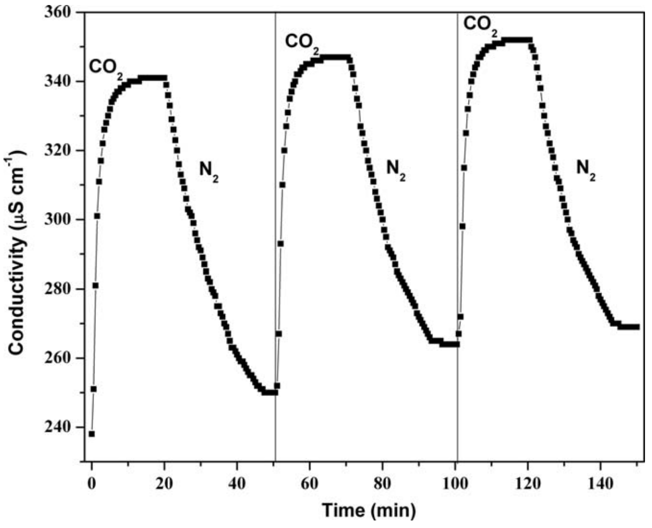


Figure 1. The conductivity of a PDAMs solution at 20°C as a function of time during three cycles of treatment with CO_2 followed by N_2.

Table I. Zeta Potential and Effective Diameter Data of PDAMs Solutions After Treated with CO_2 and N_2 (10 mg mL^{-1})

Sample		PDAM10	PDAM20	PDAM30	PDAM40	PDAM50	PDAM60	PDAM70
zeta potential (mv)	Original	−10.5	−23.3	−26.1	−13.3	−3.3	11.6	11.5
	After CO_2	−7.6	−13.6	−16.5	24.6	23.4	28.2	31.1
	After N_2	−10.1	−21.6	−23.9	−16.2	1.7	13.3	13.9
Effective Diameter (nm)	Original	12098.9	12987.1	13448.5	785.2	351.5	740.3	797.8
	After CO_2	7434.5	8674.9	10354.2	8605.1	7017.1	7543.8	7816.4
	After N_2	11978.4	13015.6	13581.7	749.8	362.2	732.6	762.9

All solutions were subjected to 20 min of CO_2 and after with nitrogen were bubbled for 30 min at a flow rate of 300 mL min^{-1}.

groups is formed in the solutions of $PDAM_{40}$, $PDAM_{50}$, $PDAM_{60}$, and $PDAM_{70}$ with high concentration of DMAEMA, which leads to the improved particle-size. PDAMs molecular micelles display an assembly-disassembly course by the addition and removal of CO_2 and it caused a hydrogel volume transition which may results in the change of its solution viscosities.

Thermo-Sensitive Property of PDAMs

DMAEMA is a well-known thermo-sensitive monomer. When the temperature is over, its lower critical solution temperature (LCST), the transition happens from a soluble (hydrated) to an insoluble (dehydrated) state and it will separate out of water. Many researchers[11,28] have reported that, poly-DMAEMA or copolymers of DMAEMA and other thermo-sensitive monomers reacts directly with CO_2 in water, which can increase drastically its LCST, namely, LCST shifts during heating and cooling, and its LCST can be influenced by the reaction with CO_2 and its removal. To exclude the effect of thermo-sensitivity on the property of CO_2-response of PDAMs, the results of transmittance measurement are tested and shown in Figure 2. In this work, DMAEMA and AM were copolymerized with varying monomer ratio, and the results of transmittance measurement indicate PDAMs is nonthermo-sensitive. Because there is no apparent hydration–dehydration transition happens during heating and cooling process. However, as temperatures rise from 20 to 80°C, the transmittance of $PDAM_{50}$ dropped from 63.8 to 10.4%. This sample shows an obvious change in transmittance because of their nontransparent initial state. It can be concluded that $PDAM_{10}$, $PDAM_{20}$, $PDAM_{30}$, $PDAM_{40}$, $PDAM_{60}$, and $PDAM_{70}$ are nonthermo-sensitive solutions and their CO_2-switchable properties would not be influenced by temperature.

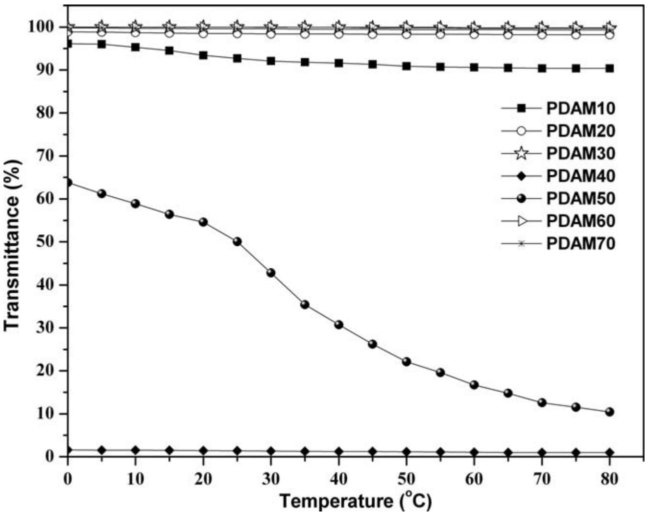


Figure 2. Transmittance versus temperature for original aqueous solutions of PDAMs.

Molecular Weights of PDAMs

The molecular weights of polymers are usually used as important and useful information in explaining rheology and the results of molecular weight for PDAMs are given in Table II. The molecular weight value of $PDAM_{10}$, $PDAM_{20}$, $PDAM_{30}$, and $PDAM_{40}$ decreased gradually. However, the molecular weight value of $PDAM_{40}$, $PDAM_{50}$, $PDAM_{60}$, and $PDAM_{70}$ is very close. As we all know, AM is easy to polymerize in aqueous solutions, when the concentration of AM is high in the course of copolymerization AM with DMAEMA, the polymerization performed more easily and the molecular weight increased. Above all, most of the molecular weight of PDAMs is close and the viscosity variation of each group of PDAMs in the cycle of bubbling with CO_2 and N_2 would not be influenced by its molecular weight. Result of molecular weight and its distribution for PDAMs are given in the supporting information.

CO_2/N_2 Switchable Viscosity-Response Properties

Viscosity of PDAMs is related to the polymer molecular structure in the solution. The tertiary amine groups in PDAMs experience a transition from an insoluble to a soluble state upon CO_2 addition. Before bubbling with CO_2, tertiary amine groups keep in the hydrophobic state and intermolecular hydrophobic association is formed. Viscosity versus concentration for original PDAMs solutions at 20°C is shown in Figure 3; before bubbling with CO_2, with the increasing concentration of solution, the viscosity of $PDAM_{10}$, $PDAM_{20}$, and $PDAM_{30}$ increased rapidly while the $PDAM_{40}$, $PDAM_{50}$, $PDAM_{60}$, and $PDAM_{70}$ maintain at a certain value like viscosity of pure water. The intermolecular hydrophobic associations are formed in $PDAM_{10}$, $PDAM_{20}$, and $PDAM_{30}$ solutions and the association effect is strengthened by the increase of concentration of DMAEMA. On the contrary, when the concentration of DMAEMA is more than 40%, the copolymer molecules are easy to curl because of the reduced polymer water-solubility and the viscosity of the corresponding copolymer solutions maintains at a certain value.

The Viscosity Variation of $PDAM_{10}$, $PDAM_{20}$, and $PDAM_{30}$. The concentration of $PDAM_{10}$, $PDAM_{20}$, and $PDAM_{30}$ is fixed at 10 mg mL^{-1}, after treated with CO_2, an obvious drop of

Table II. Molecular Weights of PDAMs

Sample	M_n	M_w	M_z	M_{z+1}	Polydispersity
$PDAM_{10}$	414731	675233	846712	945568	1.628121
$PDAM_{20}$	479265	558396	641492	719281	1.165112
$PDAM_{30}$	386469	494315	602532	696901	1.279055
$PDAM_{40}$	221081	391419	553234	681246	1.770479
$PDAM_{50}$	178649	334772	497443	623075	1.873911
$PDAM_{60}$	180223	340676	561971	716971	1.890303
$PDAM_{70}$	217159	328971	435458	525624	1.514885

viscosity happened. After bubbling with N_2, the viscosity improved to the value close the initial. As the temperature improves from 20 to 60°C, take $PDAM_{10}$ as an example [Figure 4(a)], the viscosity value of $PDAM_{10}$ decreased but it still presented an analogous viscosity change curves at 20, 40, and 60°C in the cycle of bubbling with CO_2 and N_2. When the temperature is fixed at 20°C, take $PDAM_{30}$ as an example [Figure 4(b)], with the concentration of $PDAM_{30}$ enhance from 5 to 15 mg mL^{-1}, after treated with CO_2, an obvious drop of viscosity happened. The higher the concentration of $PDAM_{30}$ is, the much more viscosity loss. After bubbling with N_2, the viscosity improved to the value close the initial. However, when the concentration of the solution is lower than 10 mg mL^{-1}, the solution viscosity increased to only half of the original.

Considering the results of conductivity, zeta potential and laser particle-size analysis above, before bubbling with CO_2, an intermolecular "self-assembling" structure was established in the solutions of $PDAM_{10}$, $PDAM_{20}$, and $PDAM_{30}$, respectively. By passing CO_2 through the solution, the raised conductivity shows that the tertiary amine group in copolymer was protonated, namely, the intermolecular hydrophobical aggregation are broken into intramolecular association, and the particle-size decreased. PDAMs molecular micelles display an assembly–disassembly course by the addition and removal of CO_2 and it caused a hydrogel volume transition which results in the drop first and rise followed of its solution viscosities.

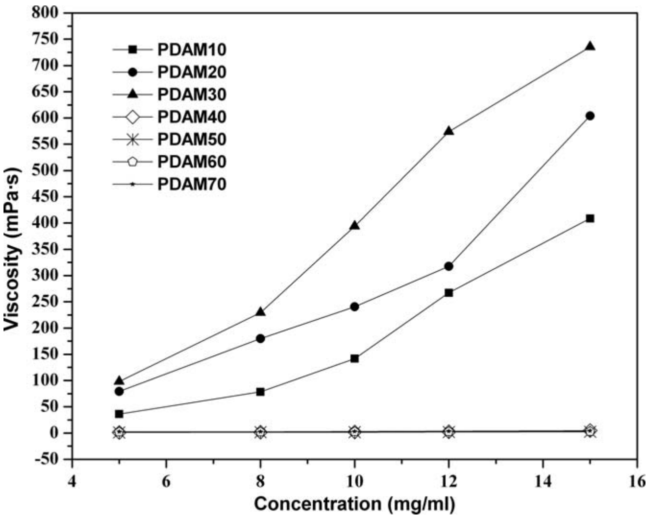


Figure 3. Viscosity versus concentration for original PDAMs solutions at 20°C.

The Viscosity Variation of $PDAM_{40}$, $PDAM_{50}$, $PDAM_{60}$, and $PDAM_{70}$. The solution of $PDAM_{40}$, $PDAM_{50}$, $PDAM_{60}$, and $PDAM_{70}$ presents a conversely CO_2/N_2 switchable viscosity-

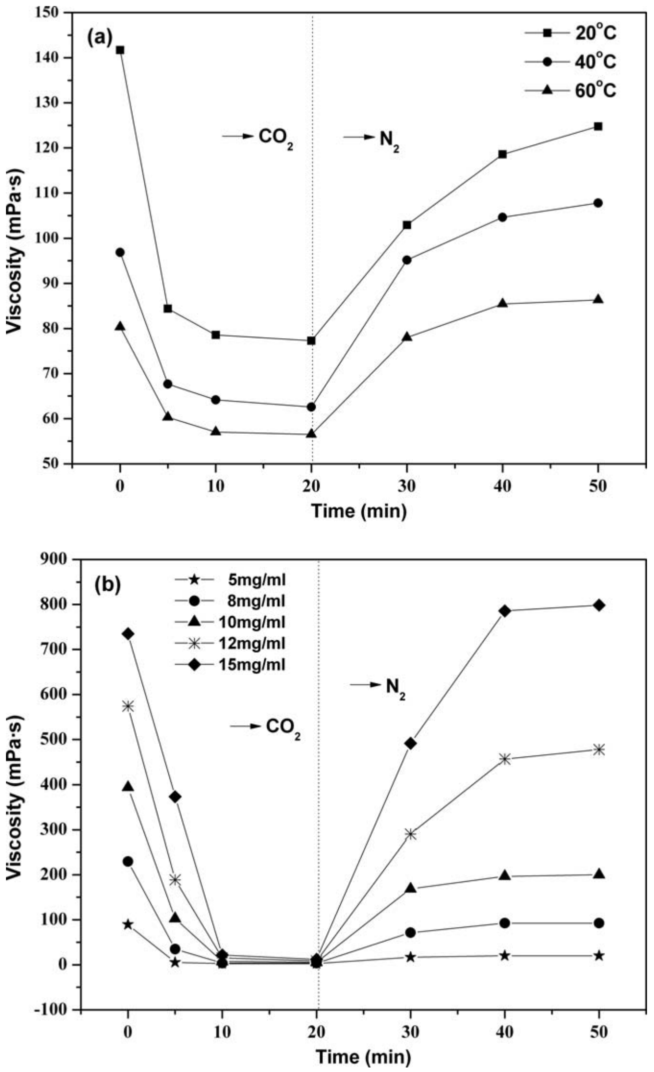


Figure 4. Viscosity variation of PDAMs in the cycle of blubbing with CO_2 followed by N_2. (a) Viscosity versus temperature for $PDAM_{10}$. (b) Viscosity versus concentration for $PDAM_{30}$.

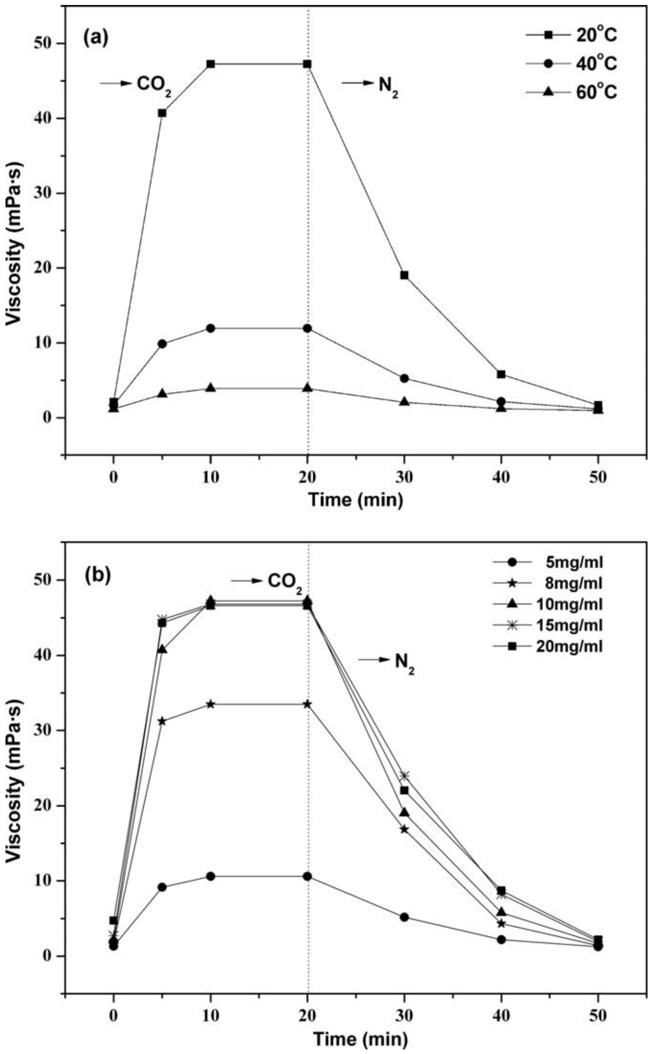


Figure 5. Viscosity variation of $PDAM_{40}$ in the cycle of blubbing with CO_2 followed by N_2. (a) Viscosity versus temperature for $PDAM_{40}$. (b) Viscosity versus concentration for $PDAM_{40}$.

response variation compared with $PDAM_{10}$, $PDAM_{20}$, and $PDAM_{30}$. Before treated with CO_2, the viscosity of $PDAM_{40}$, $PDAM_{50}$, $PDAM_{60}$, and $PDAM_{70}$ solution is very low because of high concentration of DMAEMA in copolymers leads to the poor water-solubility of PDAMs. By bubbling with CO_2 and N_2, the $PDAM_{40}$ experience a special viscosity-response variation. When the concentration of $PDAM_{40}$ is fixed at 10 mg mL^{-1}, as shown in Figure 5(a), the viscosity of $PDAM_{40}$ is improved obviously at 20°C after treated with CO_2; however, when the temperature enhanced to 40 or 60°C, there is no obvious improvement of viscosity. At 20°C, when the concentration of $PDAM_{40}$ enhance from 5 to 20 mg mL^{-1}, as shown in Figure 5(b), after treated with CO_2, an obvious rise of viscosity happened. The higher the concentration of $PDAM_{40}$ is, the much more viscosity improved. When the concentration is over 10 mg mL^{-1}, the viscosity of $PDAM_{40}$ and its varying law is close to each other. After bubbling with N_2, the viscosity decreased to the value close to the initial. By passing CO_2 through the solution, the tertiary amine group in copolymer was protonated.

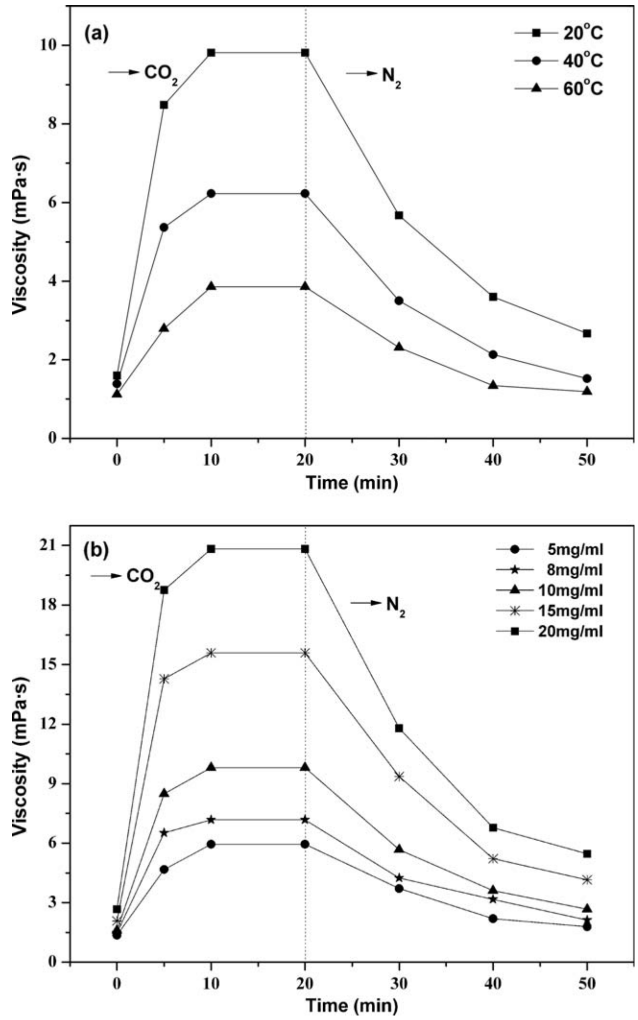


Figure 6. Viscosity variation of PDAMs in the cycle of blubbing with CO_2 followed by N_2. (a) Viscosity versus temperature for $PDAM_{50}$. (b) Viscosity versus concentration for $PDAM_{50}$.

Fuoss[31] proposed that, with the increased solution concentration of polyelectrolyte, the repulsion force in polymer molecule chains was shielded and the polymer chain nearly to be neutral. When the solution concentration of $PDAM_{40}$ is higher than 10 mg mL^{-1}, the shielded repulsion force between molecules enhanced by the counter ion and the solution viscosity showed no rising with the increase of solution concentration.

The solution of $PDAM_{50}$, $PDAM_{60}$, and $PDAM_{70}$ displayed a similar viscosity-response variation in the cycle of bubbling with CO_2 and N_2. After treated with CO_2, the protonated amine groups in the polymer molecule chains generated a strongly repulsive force against the counter ion and it make the polymer molecules stretched even at a high concentration. More importantly, the solution of $PDAM_{50}$, $PDAM_{60}$, and $PDAM_{70}$ presented an obviously viscosity change variation in the cycle of bubbling with CO_2 and N_2 even at a higher temperature (60°C). For instance, when treated with CO_2, the solution viscosity of $PDAM_{50}$ (10 mg mL^{-1}) rose from 1.8 to 9.8 mPa s and dropped to 2.6 mPa s at 20°C. When heated to 60°C, the solution viscosity of $PDAM_{50}$ dropped to 3.9 mPa s [Figure 6(a)]. When the concentration increased from 5 to 20 mg mL^{-1}, the viscosity of protonated $PDAM_{50}$ solution increased gradually from 5.9 to 20.8 mPa s [Figure 6(b)]. By bubbling with N_2, the solution properties of $PDAM_{50}$, $PDAM_{60}$, and $PDAM_{70}$ turn back to its original states. The viscosity properties data of $PDAM_{10}$, $PDAM_{20}$, $PDAM_{30}$, $PDAM_{60}$, and $PDAM_{70}$ are given in the supporting information.

CONCLUSION

A series of copolymers PDAMs were synthesized with varying monomer ratio of AM and DMAEMA in this study. The resulting copolymer solution shows an interesting property of viscosity-response which is CO_2-triggered and N_2-enabled. Tertiary amine groups of PDAMs experience a reversible transition between hydrophobical and hydrophilic state upon CO_2 addition and its removal, which induced different rheological behaviors. By passing CO_2 through the solution, the viscosity of $PDAM_{10}$, $PDAM_{20}$, and $PDAM_{30}$ decreased dramatically while the $PDAM_{40}$, $PDAM_{50}$, $PDAM_{60}$, and $PDAM_{70}$ got an obvious increase in their solution viscosity. The viscosity variation of PDAMs solutions indicated that, when the content of hydrophobic monomer of DMAEMA in hydrophilic macro chains are less than 30%, the intermolecular hydrophobic association can be destroyed by the protonated tertiary amine, which leads to the decrease of its solution viscosity. In contrast, when the increase concentration of DMAEMA is over 40%, the viscosity of PDAMs solution increased because of the protonated tertiary amine, the repulsive force in the molecule chain makes the molecules more stretched. Additionally, the viscosity properties of all the groups of PDAMs turn back nearly to the initial upon N_2 addition.

The viscosity properties of PDAMs may be allowed for a wider application. We expect that with further research, the PDAMs could be used as a novel efficient viscosity-controlled thickener for enhanced oil recovery. Meanwhile, the PDAMs enable to operate in cycling and automatically increasing or decreasing its solution viscosity to the designed value by a simple stimulation. These advantages make it more environmental friendly and reduce largely in cost.

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