Polym. Bull. (2009) 63:709–722
DOI 10.1007/s00289-009-0160-x

ORIGINAL PAPER

Solution microstructure of a micro-crosslinked acrylamide-based terpolymer

Chuanrong Zhong · Taotao Luo · Jun Deng

Received: 21 April 2009 / Revised: 13 July 2009 / Accepted: 6 September 2009 /

Abstract The hydrophobically associating copolymer poly (acrylamide/butyl styrene/sodium 2-acrylamido-2-methylpropane sulphonate) (PASA) is micro-crosslinked with a small amount of phenolic aldehyde (PL) to obtain the micro-crosslinked polymer PASA–PL with excellent liquidity and water solubility. After crosslinked, the critical association concentration of copolymer reduces in the brine solution with high NaCl concentration and PASA–PL displays much better thickening and anti-aging properties in brine solutions at low polymer concentrations. The contribution of micro-crosslink of PASA with PL to the associating structures is investigated by fluorescent probe and scanning electron microscope (SEM). The fluorescent probe results show that a large amount of hydrophobic microdomains with very strong non-polarity are formed because of greatly strengthened intermolecular hydrophobic association for the PASA–PL polymer in aqueous and brine solutions, and PASA and NaCl concentration greatly influence intermolecular hydrophobic association in PASA–PL brine solutions. SEM measurements show that continuous associative structures with huge sizes are formed in PASA–PL aqueous and brine solution.

Keywords Acrylamide · Fluorescent probe · Scanning electron microscope · Hydrophobic association · Viscosity

Introduction

The flooding polymers widely applied in enhanced oil recovery (EOR) are partially hydrolyzed polyacrylamide (HPAM) with superhigh molecular weight and

---

C. Zhong (✉) · T. Luo · J. Deng
State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation,
Chengdu University of Technology, Chengdu 610059, Sichuan, China
e-mail: zhchrong2006@yahoo.com.cn

acrylamide-modified polymers. However, the maximum applied temperature of these polymers in oil reservoirs is presently not higher than 85 °C. For high-permeability oil reservoirs, in order to improve temperature resistance, the HPAM polymer is generally micro-crosslinked with a small amount of organic trivalent aluminum, organic trivalent chromium, aldehydes, phenols, etc. [1–3]. However, while the linear HPAM with superhigh molecular weight is micro-crosslinked, the polymer gel with too high molecular weight is easily formed. As a result, the micro-crosslinked polymer dehydrates in brine solutions and pore throats in the oil reservoirs are likely to be plugged up. Moreover, the micro-crosslinked HPAM also oxidatively degrades above 85 °C, resulting in the abrupt decrease in solution viscosity. To obtain the flooding polymer whose solution properties are accordant with the expected molecular structure and properties of polymeric oil-displacing agent applied in high-permeability oil reservoirs with high salinity and temperature ($\geq$85 °C), the hydrophobically associating copolymer poly [acrylamide (AM)/butyl styrene (BST)/sodium 2-acrylamido-2-methylpropane sulphonate (NaAMPS)] (abbreviation: PASA) with low molecular weight is micro-crosslinked with a small amount of phenolic aldehyde (PL), and so the micro-crosslinked polymer PASA–PL with excellent liquidity and water solubility were synthesized. For the PASA polymer, above the critical associated concentration (C_p*) in aqueous solution, the polymer molecules can aggregate to form reversible supermolecular associating structures via intermolecular association of hydrophobic groups, resulting in a dramatical increase in apparent viscosity. Upon shearing, the associating structures are disrupted and the degradation of polymer does not occur. However, upon removal of shearing, the association can reform, resulting in the absolute recovery of polymer solution viscosities. The PASA polymer also exhibits good solution behavior such as salt-thickening, anti-aging, and temperature-thickening below 40 °C [4]. However, C_p* of PASA is on the high side in brine solutions, the viscosity below C_p* is low because of low molecular weight, and the apparent viscosities remarkably reduce above 50 °C due to destroying of the intermolecular association. After micro-crosslinked with PL containing phenyl groups, the unique solution properties of PASA are further improved, and the above mentioned problems are solved due to the increase in molecular weight and the rigidity of polymer chains. In this article, we explore intermolecular hydrophobic association of PASA–PL in aqueous and brine solution by fluorescent probe and scanning electron microscope (SEM) measurements to reveal the relationship between solution properties and microstructures of hydrophobically associating micro-crosslinked polymers in solutions.

Experimental

Reagents

AM was recrystallized twice from $CHCl_3$, and 2-acrylamido-2-methylpropane sulphonate (AMPS) was purchased from Lubrizol Co. PL with low molecular weight and butyl styrene were prepared in the laboratory [5, 6]. Other reagents were analytically pure and used without further purification.

Instrumentation

The UV spectrum was obtained with a UV-240 spectrophotometer. The FT-IR spectrum was conducted with a NICOLET-560 FT-IR spectrophotometer by using KBr disks. The purified PASA copolymer solution in D_2O was measured by a 400 MHz INOVA-400 instrument to obtain the ^{1}H-NMR spectrum. Fluorescence spectra were recorded on a Hitachi-7000 spectrophotofluorometer at 45 °C, and the pyrene concentration in the polymer solutions was 3×10^{-5} mol L^{-1}. The carbon, nitrogen, and hydrogen contents of the PASA polymer were determined by CARLO ESRA-1106 elemental analyzer.

The apparent viscosities of polymer solutions were measured by a Brookfield DVIII R27112E viscometer at the shear rate of 7.34 s^{-1} at 45 °C. The intrinsic viscosities were measured by a 0.6 mm Ubbelohde capillary viscometer at (30.0 ± 0.1) °C and 1 mol L^{-1} sodium nitrate is used as a solvent.

The scanning electron microscope images were made by S-3000 N SEM (Hitachi, Japan). The resolution of the SEM is 3 nm, and the magnifying multiple ranges from 3 to 300,000. Polymer solutions were prepared by dissolving the purified polymer in distilled water or NaCl aqueous solution. The conductive rubber was first adhibited on a special round metal plate with the diameter of 10 mm. The polymer solution sample was then dropped on the rubber and naturally dried to form the thin film at room temperature. Finally, gold was automatically sputtered on the polymer film under high vacuum for electric conduction.

Synthesis of PASA and PASA–PL

The PASA copolymer was synthesized by the free radical micellar copolymerization [7]. A 100 mL three-necked round flask was equipped with a mechanical stirrer, nitrogen inlet and outlet. AM (5.0 g, 0.0704 mol), AMPS (1.6357 g, 0.007892 mol), and sodium dodecyl sulphate (SDS) (1.0105 g) were dissolved in 20.21 mL of distilled water and the solution was placed in the flask. NaOH was used to control the pH value of the reaction solution between 6 and 7. The mixture was stirred for 15 min and BST (0.1010 g, 6.3139×10^{-4} mol) was then added into the reaction flask. The flask was purged with N_2 for half an hour. The reactant solution was heated to 50 °C with stirring in a tempering kettle under nitrogen atmosphere, and 5.98 mL of 0.005 mol L^{-1} $K_2S_2O_8$ solution was then added into the reactant solution. After the polymerization proceeded for 16 h at 50 °C, the reaction mixture was diluted with 500 mL of distilled water, and two volumes of acetone was then added with stirring to precipitate the polymers. The polymers were washed with acetone twice and extracted with ethanol by the Soxhlet extraction instrument for 2 days to remove surfactant, residual monomers and initiator. Finally, the polymers were dried under vacuo at 50 °C for 3 days.

The main component of PL with low molecular weight is 2,4,6-trimethylolphenol. PL used as the crosslinking agent was added into the PASA solutions, and the pH values of the mixtures were adjusted between 8 and 11. The mixtures were placed in the color comparison tubes. After sealed with rubber stopples and medical rubberized fabric, the tubes were placed in the constant temperature oven, and the crosslinking reaction proceeded for 3–4 days at 90 °C to obtain the micro-crosslinking polymer PASA–PL.

The molecular structures of PASA and PASA–PL are shown in Fig. 1. The intrinsic viscosities of PASA is 6.72 dL^{-1} g and the molar composition of the polymer is AM:NaAMPS:BST = 88.33:10.65:1.02. There is a typic absorption peak at 230 nm attributed to the phenyl group for the UV spectrum of PASA. FT-IR peaks of PASA (cm^{-1}) are: –N–H stretch, 3433; C=O stretch, 1647; $-CH_3$, $-CH_2$, –CH stretch, 2863, 2928, 2787; $-CH_3$, $-CH_2$, –CH bending, 1455, 1354, 1325; =C–H in phenyl stretch, 3090; $-SO_3^-$:1205, 1120, 1041, 634. Besides the above peaks of PASA, FT-IR peaks of PASA–PL (cm^{-1}) include –OH in PL stretch, 3206; –OH in PL bending, 1410; –C=C– in phenol stretch, 1612, 1560.

The observed ^{1}H-NMR (400 MHz) shifts δ (ppm) of PASA are: 4H (–CH of phenyl), 7.028–7.787; 2H ($-CH_2$ of BST main-chain), 2.105; 1H (–CH of BST main-chain), 2.772; 6H ($-CH_3$ of NaAMPS side chain), 1.674; 2H ($-CH_2$ of AMPS side chain), 3.439; 2H ($-CH_2$ of NaAMPS main-chain), 1.781; 1H (–CH of AMPS main-chain), 2.355; 2H ($-CH_2$ of AM main-chain), 1.500; 1H (–CH of AM main-chain), 2.246; H ($-NH_2$ of AM side chain and –NH of AMPS side chain), δ 4.716–4.967.

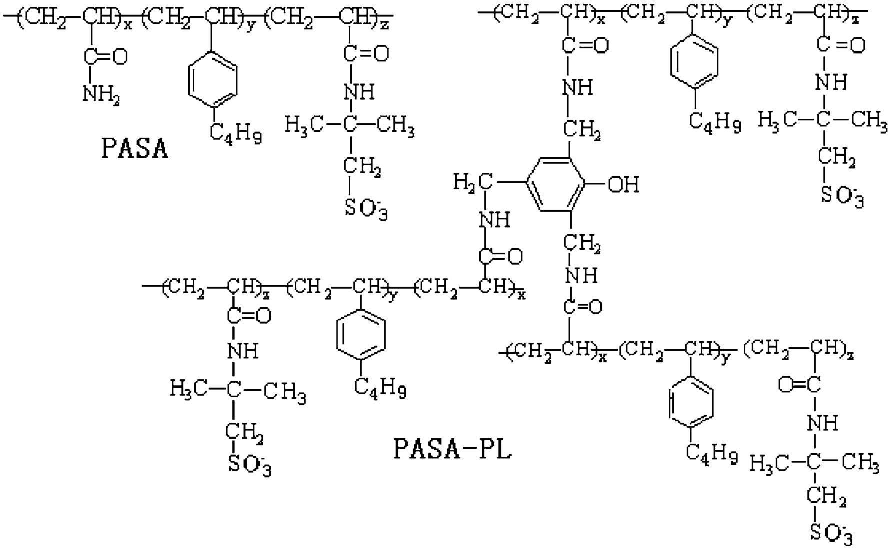

Fig. 1 Schematic representation of molecular structures of PASA and PASA–PL

Results and discussion

Effect of polymer concentration on solution viscosities

Figure 2a shows the influence of polymer concentration on apparent viscosity for the linear PASA polymer in 50 g L^{-1} NaCl solution. The solution viscosity increases sharply with increasing polymer concentration above 1.5 g L^{-1}, indicating that the critical association concentration (C_p*) is 1.5 g L^{-1}. For the micro-crosslinked polymer PASA–PL in 50 g L^{-1} NaCl solution, an obvious increase in solution viscosity with increasing polymer concentration is exhibited in Fig. 2b above 0.7 g L^{-1} which is C_p*. The result shows that the PASA polymer is micro-crosslinked with PL to result in the obvious decrease of C_p* and the great increase in solution viscosities. The micro-crosslink of PASA with PL can increase the molecular weight of polymer and improve the rigidity of polymer chains, and consequently intermolecular hydrophobic association and viscosification effect of the polymers in brine solution are strengthened, leading to high solution viscosities at low polymer concentrations.

Effect of NaCl concentration on solution viscosities

The plot of apparent viscosity of the PASA–PL brine solution versus NaCl concentration is displayed in Fig. 3a. With increasing NaCl concentration, the solution viscosity of PASA–PL with 1.0 g L^{-1} PASA and 0.3 g L^{-1} PL first decreases, then sharply increases, and finally begins to decrease above 10 g L^{-1} NaCl. In the range of 2–5 g L^{-1} NaCl, charge shielding effect of Na^+ on $-SO_3^-$ groups along the polymer chain results in coiled molecular conformation and weakened intermolecular hydrophobic association, and with the increase of NaCl concentration from 5 to 10 g L^{-1}, the solution polarity induced by electrolytes increases, resulting in reinforced intermolecular association of the hydrophobic groups and the good salt-thickening behavior of the PASA–PL polymer. With the further increase in NaCl concentration, the associating microstructures turn more

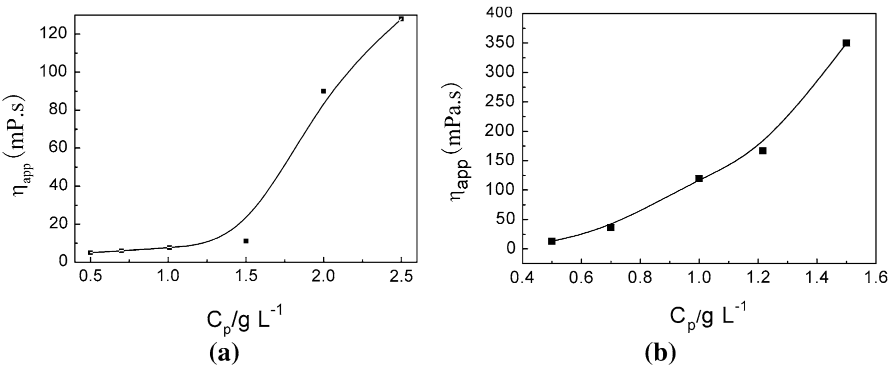

Fig. 2 Influence of polymer concentration on apparent viscosities for PASA and PASA–PL in 50 g L^{-1} NaCl solution: **a** PASA; **b** PASA–PL

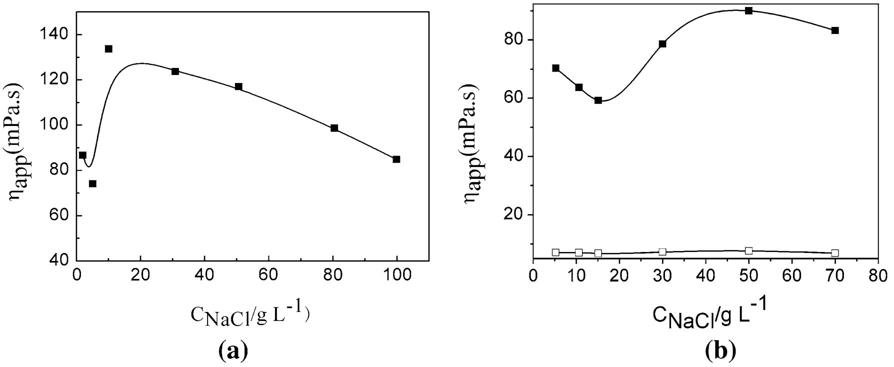

Fig. 3 Influence of NaCl concentration on apparent viscosities of polymer brine solutions: **a** PASA–PL (*filled square* PASA concentration: 1.0 g L^{-1}); **b** PASA (*filled square* 2.0 g L^{-1}, *open square* 1.0 g L^{-1})

compact and the apparent viscosity decreases. However, the apparent viscosity still reaches 85 mPa s at 100 g L^{-1} NaCl. Figure 3b shows the electrolytical effect of the linear PASA polymer. Compared with PASA–PL, the similar influence tendency of NaCl on apparent viscosity is displayed for the 2.0 g L^{-1} PASA polymer solution, but the maximum viscosity (134 mPa.s) of 1.0 g L^{-1} PASA–PL brine solution is higher than that (90 mPa.s) of 2.0 g L^{-1} PASA solution. For the 1.0 g L^{-1} PASA polymer solution, the apparent viscosity tends to be constant over the range of NaCl concentration because of the very weak intermolecular hydrophobic association below C_p* (1.5 g L^{-1}).

Aging effect

Figure 4a displays the variation of apparent viscosity with aging time at 90 °C for the linear 1.0 g L^{-1} PASA polymer in 50 g L^{-1} NaCl solution with saturated oxygen. After aging for 30 days, the apparent viscosity of the brine solution reduced from 9.8 to 6.4 mPa s and the viscosity retention ratio is 65.3%. The apparent viscosity almost remains invariable after the brine solution was further aged for 60 days. Figure 4b displays the plot of apparent viscosity versus crosslinking and aging time at 90 °C for the PASA–PL polymer with 1.0 g L^{-1} PASA and 0.3 g L^{-1} PL in 50 g L^{-1} NaCl solution with saturated oxygen. As shown in Fig. 4b, the apparent viscosity of the PASA–PL brine solution increases to 45.5 mPa s after crosslinking for 1 day, then sharply increases to 119.1 mPa s as further crosslinking for 3 days. After 4 days pass, the crosslinking reaction is over and the apparent viscosity begins to decrease. The apparent viscosity reduces from 119.1 to 103.6 mPa s after aging for 26 days, and the viscosity retention ratio is 87.0%. The apparent viscosity almost remains constant with the further increase of aging time. The results show that the anti-aging properties of the PASA–PL polymer is excellent in comparison with the linear PASA polymer at low polymer concentration at 90 °C. These results also reveal that the PASA–PL polymer can be applied in the oil reservoirs with the temperature higher than 85 °C and high salinity. The excellent thermal stability of the PASA–PL brine solution is due to the

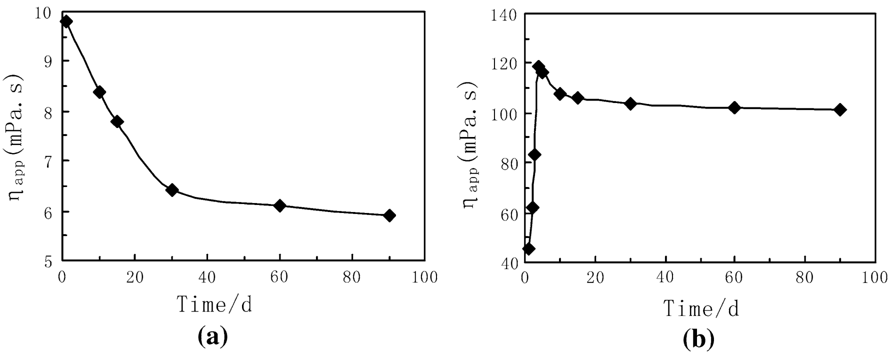

Fig. 4 Influence of aging time on apparent viscosities of polymer brine solutions. PASA concentration: 1.0 g L^{-1}; NaCl concentration: 50 g L^{-1}. **a** PASA; **b** PASA–PL

incorporation of the rigid bulky pendant side groups into crosslinking polymer chains. These groups include phenyl groups, (4-butyl) phenyl groups and 2-acrylamido-2-methylpropane sulphonate groups, which are stable and can effectively interfere with the hydrolysis of amido groups in the polymers and oxidative degradation of polymer chains.

Influence of micro-crosslink on hydrophobic association

In order to explore the contribution of micro-crosslink of PASA with PL to the supermolecular associating structures, the fluorescent probe technique is used for investigating the formation of hydrophobic microenvironment, and the probe is commonly pyrene, whose solubility in water is very low (about 1.0×10^{-7} mol L^{-1}) and is preferably solubilized into hydrophobic microdomains. Among the various fluorescent probes, the vibrational fine structure of emission spectrum for pyrene is most sensitive to the change in located microenvironment [8–11], and the intensity ratio I_1/I_3 of the first (375 nm) to the third (384 nm) vibronic peaks in the fluorescence emission spectrum is sensitive to the polarity of the local microenvironment of the pyrene probe. Thus, the formation of hydrophobic microdomains in aqueous solution can be evidenced by a decrease of I_1/I_3 value, and the lower I_1/I_3 value is, the stronger the non-polarity is.

The pyrene emission spectrum is shown in Fig. 5a for 1.5 g L^{-1} PASA aqueous solution, and according to the emission spectra, the I_1/I_3 value is 1.558 and is lower than that in pure water (1.76) [12]. The result indicates that hydrophobic microdomains are formed via intermolecular van der walls interaction of (4-butyl) phenyl groups at the polymer concentration of 1.5 g L^{-1}. As shown in Fig. 5a, a broad featureless spectral emission peak occurs at about 475 nm, and the peak is also called the pyrene excimer emission peak (intensity I_e). The fluorescent emission spectrum of the excited pyrene in the absence of pyrene–pyrene interactions consists of major peaks at 375, 384, and 399 nm (monomer emission peak, intensity I_m), and only when the concentration of pyrene in the hydrophobic

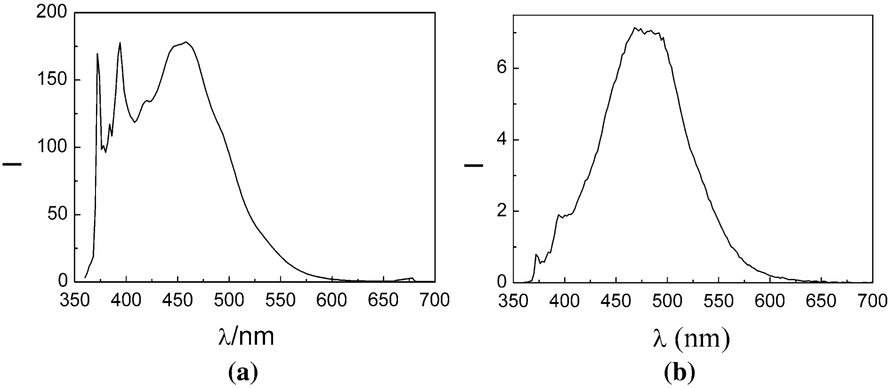

Fig. 5 Fluorescence spectra of pyrene in PASA and PASA–PL aqueous solutions. Polymer concentration: 1.5 g L^{-1}. **a** PASA aqueous solution; **b** PASA–PL aqueous solution

microenvironment is high enough for an excited pyrene (Py*) and a pyrene in its ground state to come into close proximity during the Py* lifetime, pyrene excimers are formed. Hence, the I_e/I_m ratio has often been used as an indicator of the degree of interaction between fluorophores [13]. For hydrophobically associating polymer, the I_e/I_m ratio provides a measure to characterize the association degree of hydrophobic segments on the polymer chains and microviscosity of hydrophobic microdomains. For 1.5 g L^{-1} PASA aqueous solution, the I_e/I_m value is 1.118, indicative of strong hydrophobic association. The pyrene emission spectrum is shown in Fig. 5b for the PASA–PL polymer aqueous solution with 1.5 g L^{-1} PASA and 0.3 g L^{-1} PL. The I_1/I_3 value is 0.948 and is greatly lower than that in PASA aqueous solution. The I_e/I_m value is 3.717 and is greatly higher than that in PASA aqueous solution. In addition, the fluorescent intensity in the red brown PASA–PL aqueous solution is much lower than that in the colorless PASA aqueous solution because of fluorescent quenching in the presence of phenol. Figure 5a, b suggest that for the PASA–PL aqueous solution, a large amount of hydrophobic microdomains are formed because of increased molecular weight and reinforced hydrophobic associations, and the sizes of aggregates and the concentration of pyrene excimers dissolved in hydrophobic microdomains increase abruptly.

Figure 6a, b show the pyrene emission spectra of 1.5 g L^{-1} PASA and 1.5 g L^{-1} PASA–PL in 50 g L^{-1} NaCl solution, respectively. For 1.5 g L^{-1} PASA brine solution, the I_1/I_3 and I_e/I_m values are 1.128 and 1.524, respectively. For 1.5 g L^{-1} PASA–PL brine solution, the I_1/I_3 value is 0.848 and lower than that (0.948) in aqueous solution and that in 1.5 g L^{-1} PASA brine solution. The I_e/I_m value is 6.537 and is much higher than that (3.717) in aqueous solution and that in 1.5 g L^{-1} PASA brine solution. The fluorescent probe results indicate that the increased solution polarity by addition of NaCl makes the hydrophobic groups in the PASA–PL brine solution arrange more close, resulting in much stronger hydrophobic associations and the remarkable increase of non-polarity of hydrophobic microdomains.

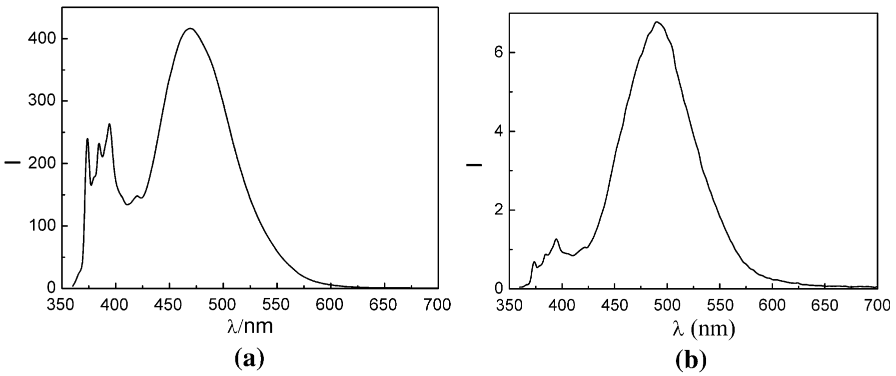

Fig. 6 Fluorescence spectra of pyrene in PASA and PASA–PL brine solutions. Polymer concentration: 1.5 g L^{-1}, NaCl concentration: 50 g L^{-1}. **a** PASA brine solution; **b** PASA–PL brine solution

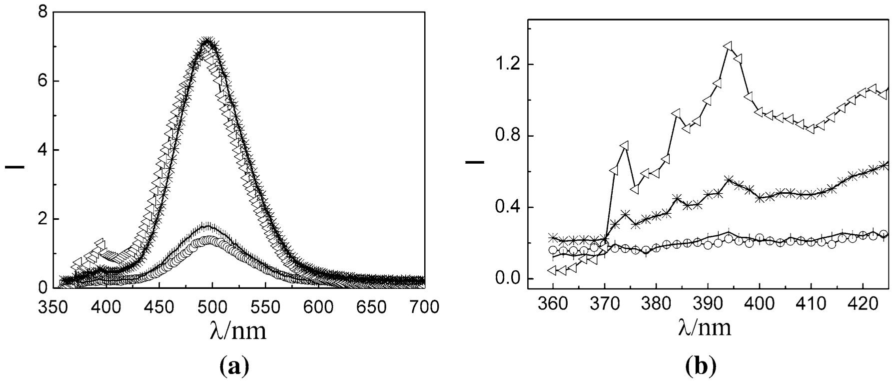

Fig. 7 Fluorescence spectra of pyrene in PASA–PL brine solutions with different PASA concentration. NaCl concentration: 50 g L^{-1}. PASA concentration: *circle* 1.0 g L^{-1}; *plus* 1.2 g L^{-1}; *triangle* 1.5 g L^{-1}; *asterisk* 2.0 g L^{-1}. **a** Whole fluorescence spectra; **b** enlarged fluorescence spectra

Effect of polymer concentration on hydrophobic association

Figure 7a shows the pyrene emission spectra for the 50 g L^{-1} NaCl solutions of PASA–PL with different PASA concentration and 0.30 g L^{-1} PL, and the pyrene emission spectra in the fluorescent wavelength range of 360–430 nm are enlarged to obtain Fig. 7b. According to above pyrene emission spectra, the plots of I_1/I_3 and I_e/I_m versus PASA concentration are, respectively, displayed in Fig. 8a, b. As shown in Fig. 8a, the I_1/I_3 value obviously decreases from 0.980 to 0.848 with increasing the PASA concentration from 1.0 to 1.5 g L^{-1}, and then slowly decreases up to 0.800 at the PASA concentration of 2.0 g L^{-1}, indicating that the non-polarity in hydrophobic microenvironment is higher than that of isopropyl ether ($I_1/I_3 = 0.88$) [14]. The variation of I_1/I_3 with PASA concentration reveals that with the increase in PASA concentration, the number of polymer chains crosslinking with PL increases, resulting in the increase in molecular weight of PASA–PL and the

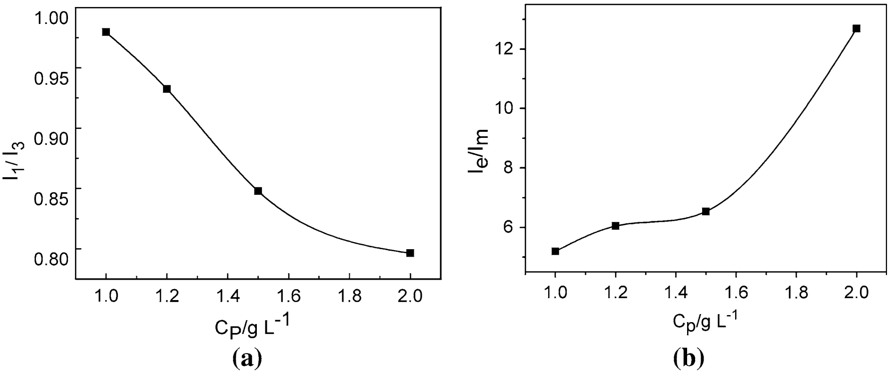

Fig. 8 Influence of PASA concentration on I_1/I_3 and I_e/I_m values in PASA–PL brine solutions. NaCl concentration: 50 g L^{-1}. **a** I_1/I_3 versus PASA concentration; **b** I_e/I_m versus PASA concentration

number of microcrosslinked polymer chains. Therefore, intermolecular hydrophobic association is remarkably strengthened. Figure 8b shows that with increasing the PASA concentration, the I_e/I_m value first gradually increases, and then abruptly rises from 6.537 at 1.5 g L^{-1} PASA to 12.690 at 2.0 g L^{-1} PASA. The result reveals that despite the slow increase in the non-polarity of hydrophobic microenvironment, the number and sizes of hydrophobic microenvironment sharply increase because of the reinforced intermolecular association of PASA–PL. Compared with Fig. 2b, the fluorescent probe results are consistent with the thickening effect of PASA–PL in brine solution.

Effect of NaCl concentration on hydrophobic association

The pyrene emission spectra are displayed in Fig. 9a, b for the PASA–PL brine solutions with different NaCl concentration, 1.5 g L^{-1} PASA and 0.30 g L^{-1} PL, where (a) is enlarged in the wavelength range of 360–420 nm to obtain (b), and the plots of I_1/I_3 and I_e/I_m versus NaCl concentration are displayed in Fig. 10a, b, respectively. As shown in Fig. 10a, with the increase in NaCl concentration from 0 to 80 g L^{-1}, the I_1/I_3 value first increases, then obviously decreases and the minimum reaches at 10 g L^{-1} NaCl, and finally increases again. However, the all I_1/I_3 values are below 0.90 in the range of 10–80 g L^{-1} NaCl. The result suggests that the non-polarity in microdomains is the strongest at 10 g L^{-1} NaCl and the number and sizes of network structures are also the largest at the NaCl concentration, resulting in the highest solution viscosity, but huge associative structures of PASA–PL are still formed above 10 g L^{-1} NaCl. Moreover, as displayed in Fig. 10b, the I_e/I_m value abruptly decreases from 3.717 to 1.950 with the increase in NaCl concentration from 0 to 5 g L^{-1}, which is due to the electrostatic shielding of intermolecular repulsions and the formation of coiled polymer chains. Thus, intramolecular association interferes with intermolecular association. The I_e/I_m value remarkably increases from 1.950 to 6.537 with increasing NaCl concentration from 5 to 50 g L^{-1}, and finally the I_e/I_m value tends to be constant above 50 g L^{-1}

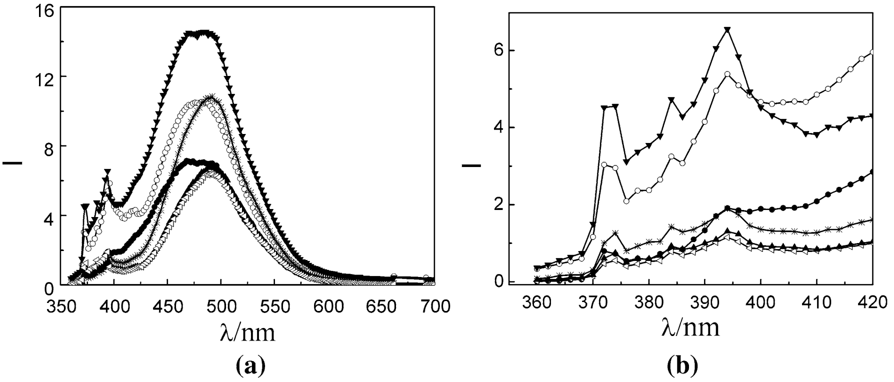

Fig. 9 Fluorescence spectra of pyrene in PASA–PL brine solutions with different NaCl concentration. PASA concentration: 1.5 g L^{-1}; PL concentration: 0.30 g L^{-1}. NaCl concentration: *filled circle* 0 g L^{-1}; *open circle* 5 g L^{-1}; *filled inverted triangle* 10 g L^{-1}; *asterisks* 30 g L^{-1}; *filled triangle* 50 g L^{-1}; *open triangle* 80 g L^{-1}. **a** Whole fluorescence spectra; **b** enlarged fluorescence spectra

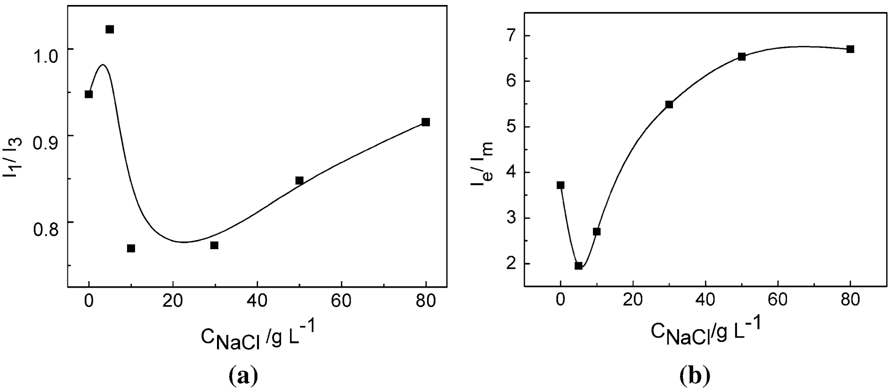

Fig. 10 Influence of NaCl concentration on I_1/I_3 and I_e/I_m values in PASA–PL brine solutions. PASA concentration: 1.5 g L^{-1}; PL concentration: 0.30 g L^{-1}. **a** I_1/I_3 versus NaCl concentration; **b** I_e/I_m versus NaCl concentration

NaCl. Figure 9 shows that the non-polarity of microdomains slightly decreases above 10 g L^{-1} NaCl, but the compact degree of associative microdomains increases, resulting in the increase in pyrene dissolved in the microdomains.

Associating morphologies of PASA–PL

Figure 11a shows associative morphologies of 1.5 g L^{-1} PASA in aqueous solution, and the three-dimensional networks are formed because of intermolecular hydrophobic association. Continuous associative structures with huge sizes are formed via micro-crosslink of 1.5 g L^{-1} PASA with PL (Fig. 11b). After the PASA polymer is

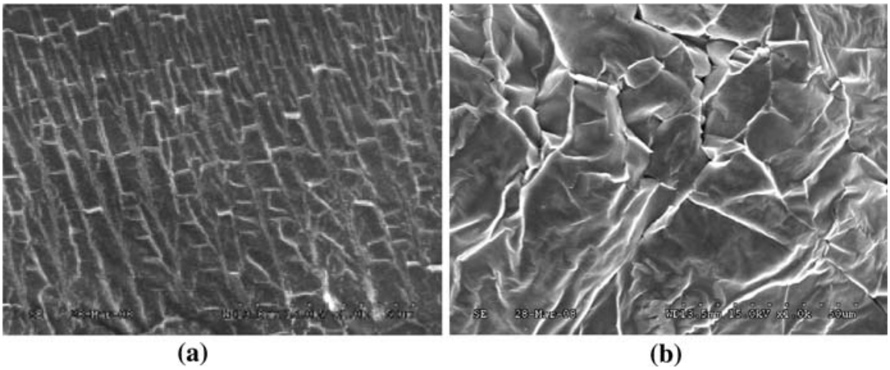

Fig. 11 SEM images of PASA and PASA–PL aqueous solution with 1.5 g L^{-1} PASA: **a** PASA (×1000); **b** PASA–PL (×1000)

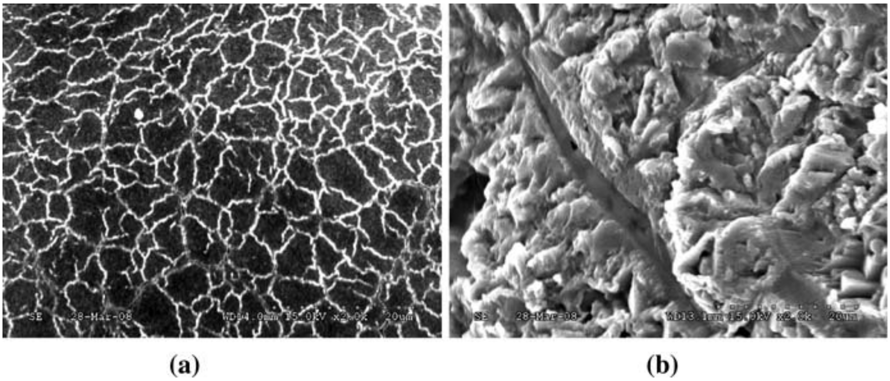

Fig. 12 SEM images of 1.5 g L^{-1} PASA–PL in brine solutions: **a** 5 g L^{-1} NaCl (×2000); **b** 50 g L^{-1} NaCl (×2000)

micro-crosslinked, the molecular weight obviously increases and intermolecular hydrophobic association are strengthened, resulting in high apparent viscosity of PASA–PL aqueous solution.

Figure 12a displays continuous network structures of 1.5 g L^{-1} PASA–PL in 5 g L^{-1} NaCl solution. However, our previous studies show that continuous associative network structures cannot be yet formed in brine solution at the high PASA concentration of 5 g L^{-1} [12]. Compared with PASA, the rigidity of PASA–PL molecules becomes much stronger and the molecular weight is higher, resulting in better salt resistance and reinforced intermolecular hydrophobic association. With varying NaCl concentration from 5 to 50 g L^{-1}, the associative structures become distinctly much huger and more condensed because of strengthened association caused by increased solution polarity (Fig. 12b). The SEM images of PASA–PL are accordant with the above fluorescent probe results and solution viscosity measurement.

Conclusions

The hydrophobically associating copolymer poly (acrylamide/butyl styrene/sodium 2-acrylamido-2-methylpropane sulphonate) (abbreviation: PASA) with low molecular weight is micro-crosslinked with a small amount of phenolic aldehyde (PL) to obtain the micro-crosslinked polymer PASA–PL with excellent liquidity and water solubility. After crosslinked, the critical association concentration of copolymer reduces in the brine solution with high NaCl concentration and the apparent viscosities of brine solutions greatly increase. The PASA–PL polymer exhibits good salt resistance and excellent anti-aging property at high temperature of 90 °C. The I_1/I_3 and I_e/I_m values for the PASA–PL polymer in aqueous and brine solution indicate that intermolecular hydrophobic association is abruptly strengthened and a large amount of hydrophobic microdomains with greatly strong non-polarity are formed because of micro-crosslink. For PASA–PL in 50 g L^{-1} NaCl solution, with increasing PASA concentration, I_1/I_3 obviously decreases below 1.5 g L^{-1}, and I_e/I_m abruptly rises above 1.5 g L^{-1}. In the brine concentrations of 1.5 g L^{-1} PASA–PL, the maximum I_1/I_3 value reaches at 5 g L^{-1} NaCl due to the electrostatic shielding of intermolecular repulsion, the minimum reaches at 10 g L^{-1} NaCl, indicating that the number and sizes of network structures are the largest, and the I_e/I_m values show that the compact degree of associative microdomains increase with increasing NaCl concentration. SEM measurements show that continuous associative structures with huge sizes are formed via micro-crosslink of 1.5 g L^{-1} PASA with PL in aqueous solution and continuous network structures are still formed for 1.5 g L^{-1} PASA–PL in 5 g L^{-1} NaCl solution. With increasing NaCl concentration, the associative structures become distinctly much huger and more condensed. The fluorescent probe results are consistent with the SEM images of PASA–PL. These characterizations of solution microstructures reveal that after the PASA polymer is micro-crosslinked with PL, the molecular weight obviously increases and the rigidity of polymer chains is greatly improved, resulting in abruptly strengthened intermolecular hydrophobic association. Thus, PASA–PL brine solutions display high apparent viscosities at low polymer concentrations.

Acknowledgements We acknowledge the financial support of Open Foundation of State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation (contract grant number: PLC200601).

References

1. Grattoni CA, Al-Sharji HH, Yang CH et al (2001) Rheology and permeability of crosslinked polyacrylamide gel. J Colloid Interface Sci 240:601–607
2. Albonico P, Lockhart TP (1991) Crosslinking structure and chemistry of aqueous Cr^{3+}/polyacrylamide cells. Polym Prepr Div Polym Chem 32:610–611
3. Cai WS, Huang RH (2001) Study on gelation of partially hydrolyzed polyacrylamide with titanium(IV). Eur Polym J 37:1553–1559
4. Zhong CR, Huang RH, Zhang X et al (2007) Synthesis, characterization, and solution properties of an acrylamide-based terpolymer with butyl styrene. J Appl Polym Sci 103:4027–4038
5. Qian XL, Wu WH, Yu PZ et al (2005) Synthesis of water-soluble phenolic resin as crosslinker of polymer weak gel. Oilfield Chem 22:241–244

6. Littke AF, Schwarz LF, Gregory CJ (2002) Pd/P(t-Bu)(3): a mild and general catalyst for Stille reactions of aryl chlorides and aryl bromides. J Am Chem Soc 124:6343–6348
7. Hill A, Candau F, Selb J (1993) Properties of hydrophobically associating polyacrylamides: influence of the method of synthesis. Macromolecules 26:4521–4532
8. Wilhelm M, Zhao CL, Wang Y (1991) Poly(styrene-ethylene oxide) block copolymer micelle formation in water: a fluorescence probe study. Macromolecules 24:1033–1040
9. Chen J, Jiang M, Zhang Y et al (1999) Fluorescence studies on hydrophobic associations of fluorocarbon-modified poly(acrylic acid) solutions. Macromolecules 32:4861–4866
10. Dowling KC, Thomas JK (1990) A novel micellar synthesis and photophysical characterization of water-soluble acrylamide-styrene block copolymers. Macromolecules 23:1059–1064
11. Bromberg LE, Barr DP (1999) Aggregation phenomena in aqueous solutions of hydrophobically modified polyelectrolytes. A probe solubilization study. Macromolecules 32:3649–3659
12. Zhong CR, Ye L, Dai H, Huang RH (2007) Flourescent probe and ESEM morphologies of a acrylamide-based terpolymer in aqueous solution. J Appl Polym Sci 103:277–286
13. Winnik FM (1993) Photophysics of preassociated pyrenes in aqueous polymer solutions and in other organized media. Chem Rev 93:587–614
14. Zhong CR (2004) Study on the synthesis and properties of hydrophobically modified polyacrylamide and its associating morphology in solutions, Doctor dissertation, Sichuan University, Chengdu, China