

Article

Preparation and Evaluation of High-Temperature-Resistant Copolymer Gels for Enhanced Oil Recovery: A Study on Gelation Properties and Thermal Stability

Zhande Yang ¹, Jing Bai ¹, Yanheng Liang ¹, Mengyu Liu ¹, Bowen Chen ² and Jingwei Chen ^{3,*}

¹ Xi'an Changqing Chemical Group Co., Ltd., Xi'an 710200, China

² Shale Gas Research Institute of PetroChina Southwest Oil & Gas Field Company, Chengdu 610051, China

³ State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, China

* Correspondence: 13566826972@163.com

Abstract

In the late stage of oilfield water flooding, the rapid increase in water cut of produced fluids significantly reduces oil well productivity. To tackle the challenge of excessive water production in ultra-high-temperature (150 °C) reservoirs, this study introduces a copolymer (acrylamide/vinylpyrrolidone copolymer, acrylamide/2-acrylamido-2-methylpropanesulfonic acid copolymer)-based gel system. The gelation performance of copolymers with varying compositions and molecular weights was systematically investigated at 150 °C using gelation visualization codes, mechanical strength tests, microstructural analysis, thermogravimetric analysis (TGA), and nuclear magnetic resonance (NMR) spectroscopy. These approaches provide insights into the thermal and mechanical behavior of the gel under high-temperature conditions. Experimental results show that under optimized conditions—specifically with a vinylpyrrolidone (NVP) content of 30–40% in the copolymer and a copolymer concentration of 1.0 wt%—the gel system exhibited the best performance: a gelation time of 9.5–11 h, storage modulus (G') of 14.7–16.0 Pa, and stability exceeding 6 months at 150 °C. Moreover, increasing the molecular weight from 1.78×10^6 to 3.82×10^6 shortened the gelation time from 18.5 h to 14 h and raised the gel strength code from F to G. Although higher molecular weight led to a finer microstructure lattice and somewhat lower chemical structure stability, it also reduced the gel's water-binding capacity compared to lower-molecular-weight analogues. The copolymer gel system developed in this work offers a promising technical solution for improving water flooding efficiency in ultra-high-temperature reservoirs.

Keywords: copolymer gel; high-temperature reservoirs; gelation performance; thermal stability



Academic Editor: Ian Wyman

Received: 27 December 2025

Revised: 7 February 2026

Accepted: 12 February 2026

Published: 26 February 2026

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1. Introduction

During the late phase of water flooding, reservoir pressure maintenance becomes increasingly difficult as oil is produced. A concurrent issue is formation heterogeneity, which causes injected water to channel preferentially through high-permeability layers, leaving significant oil volumes unswept in less permeable zones [1,2]. This phenomenon leads to the rapid formation of water aggregation channels within the pore network and a consequent sharp increase in the water cut of produced fluids. Under such circumstances,

well productivity declines, and in severe cases, production may cease entirely due to economic limits [3–5]. To mitigate these issues, it is essential to implement profile modification in injection wells and conformance control in production wells to block dominant water flow paths [6,7].

In the domain of conformance control and water shutoff, chemical methods represent one of the most versatile and promising technological pathways [8]. Among these, gel-based systems are particularly notable as a widely adopted and cost-effective category of selective water control agents. Conventional gel systems typically consist of partially hydrolyzed polyacrylamide (HPAM) in combination with a crosslinking agent [9]. By adjusting the hydrolyzed charge density and molecular weight of HPAM, such systems can be engineered to crosslink effectively across a range of reservoir conditions, rendering them a reliable option for water management in moderate-temperature environments [10]. However, the deployment of these conventional gels becomes considerably constrained in high-temperature reservoirs. For example, in deep formations such as those in the Jidong and Tahe oilfields in China, reservoir temperatures can reach 140–160 °C. Under such extreme thermal conditions, HPAM undergoes pronounced thermal degradation at temperatures exceeding 80 °C [11,12]. Moreover, gels formed with conventional crosslinkers exhibit several operational limitations, including excessively short gelation times, inadequate mechanical strength, and insufficient long-term thermal stability [13]. For instance, the commonly used inorganic crosslinkers can form crosslinks through ionic or coordination bonds by reacting with the carboxyl groups of the polymer. Specifically, divalent ions such as calcium (Ca^{2+}) form ionic bonds with the carboxyl groups of the polymer, while polyvalent metal ions such as aluminum (Al^{3+}), chromium (Cr^{3+} and Cr^{6+}), and zirconium (Zr^{4+}) form coordination bonds via chelation. However, due to the limitations of the crosslinking mechanism in polymer–inorganic crosslinked gel systems, a significant number of amide groups remain in the gel after crosslinking. Under combined high-temperature and saline conditions, these unreacted amide groups may gradually hydrolyze to form carboxyl groups. These newly generated carboxyl groups can further crosslink with calcium ions present in the formation water, potentially increasing the risk of dehydration in inorganic crosslinked polymer gel systems. Consequently, the effective application window of standard HPAM-based gel systems is generally limited to temperatures below 120 °C, highlighting a critical performance gap for ultra-high-temperature reservoir environments [14,15].

The temperature resistance of polymer gels is typically enhanced by incorporating thermally stable monomers into partially hydrolyzed polyacrylamide (HPAM) or by selecting suitable crosslinking systems [16]. In pioneering work, Morgan et al. identified a gel system combining polyethyleneimine (PEI)—an organic crosslinker—with a copolymer of acrylamide and tert-butyl acrylate. This system exhibited exceptional thermal stability, withstanding temperatures up to 156 °C [17]. Xin et al. introduced an innovative approach in which an inorganic crosslinker, aluminum citrate, was first added to an HPAM solution to initiate crosslinking, followed by the incorporation of 1,3,4,6-tetrakis(hydroxymethyl) glycoluril. This two-step process produced an interpenetrating polymer network gel with high crosslinking density, thereby improving its thermal stability [18]. Moradi et al. reported several low-toxicity or non-toxic phenolic crosslinkers as alternatives to phenol. When phenylacetic acid was substituted for phenol, a stable gel formed after aging for 20 days at 120 °C. In a system using salicylic acid instead of phenol together with hexamethylenetetramine (HMTA), gelation time was considerably extended: in brine with a salinity of 2000 mg L^{−1} at 121 °C, a gel formed after 31 days, and a high-strength gel developed after 157 days [19]. Zhu et al. investigated the effects of different phenolic crosslinkers on the long-term thermal stability of polymer-gel systems at 150 °C. Their

study showed that in a P(AM/AMPS/NVP)-based gel system, the gelling performance with hydroquinone–hexamethylenetetramine (HQ–HMTA) was inferior to that with resorcinol–hexamethylenetetramine (RQ–HMTA) [16].

Conventional gel systems currently face significant limitations, including insufficient thermal resistance and inadequate long-term stability. In particular, gel systems employing inorganic crosslinkers are prone to issues such as over-crosslinking or dehydration-induced syneresis under high-temperature reservoir conditions. To address these challenges, this study proposes two novel thermally stable copolymer-based gel systems specifically designed for reservoirs with well-developed pore-fracture networks. By systematically investigating different copolymer types and molecular weights, the work elucidates the underlying mechanisms governing gelation behavior, viscoelastic moduli, gel microstructure, and thermal endurance. The outcomes of this research are anticipated to offer critical technical insights for mitigating reservoir heterogeneity, modulating water–oil mobility ratios in high-temperature settings, improving sweep efficiency in water-flooding processes, and ultimately enhancing the overall performance of water-based enhanced oil recovery.

2. Experimental Section

2.1. Chemicals

Copolymers of acrylamide with N-vinylpyrrolidone (P(AM/NVP)) and with 2-acrylamido-2-methylpropanesulfonic acid (P(AM/AMPS)) were synthesized in the laboratory, each with a solid content of 98%. Hexamethylenetetramine (HMTA), hydroquinone (HQ), and thiourea were sourced from Chengdu Kelong Co., Ltd. (Chengdu, China) and used as received without further purification. All experiments were conducted using deionized water (resistivity $\geq 18.0 \text{ M}\Omega\cdot\text{cm}$).

2.2. Experimental Method

The copolymer gel was prepared as follows: First, a measured volume of deionized water was placed into a stirrer and agitated at 400 rpm. A predetermined amount of copolymer powder was then weighed and gradually added to the water under continuous stirring to avoid the formation of “fish-eye” aggregates, yielding a homogeneous base solution. After 4 h of hydration, the polymer solution was diluted to target concentrations of 0.8 wt% and 1.0 wt%. The relatively high concentrations were used due to the copolymer’s relatively low molecular weight and the high-temperature resistance requirement of the gel. During dilution, crosslinker (HMTA, HQ) and oxygen scavenger (thiourea) were incorporated to formulate the final gel system. The mixture was transferred into a high-pressure glass bottle, purged with nitrogen for 30 min, and then sealed. Gelation was carried out under static conditions at 150 °C. The reaction pathway of the crosslinking agent with the copolymer was illustrated in Figure 1.

Gelation performance was evaluated according to the Sydansk visual code method. An alphabetic code of A through I was used to characterize gel strength wherein A–E represent flowing gels, F–H refer to non-flowing gels, and I–J signify rigid gels (Figure 2) [20,21]. Because high-strength gels resemble solids rather than liquids, traditional viscosity measurements tend to be prone to distortion and are often unsuitable, thus visual methods are commonly employed to directly assess their yield stress—an approach that aligns more closely with practical operating conditions and offers greater engineering utility. The dehydration rate of the gel was determined by measuring the volume of expelled water over time, expressed as the ratio of water loss to the initial gel volume at designated aging intervals [22].

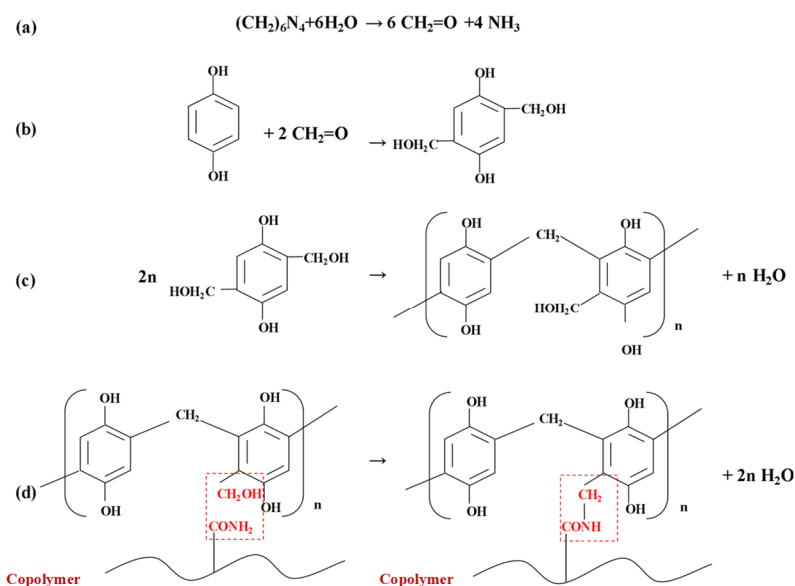


Figure 1. Crosslinking reaction scheme.

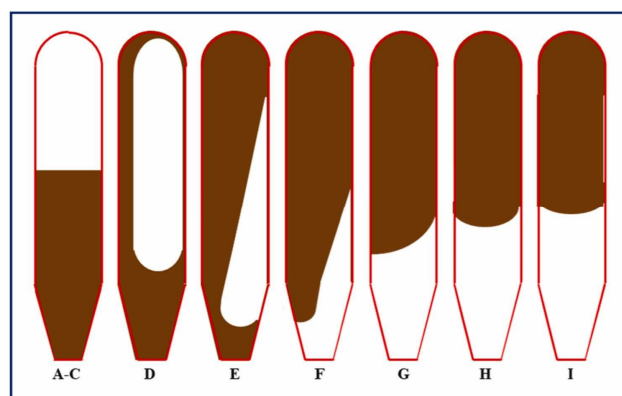


Figure 2. Illustration of Sydansk's gel strength code.

Further rheological characterization was performed using an MCR 302 rheometer (Physica). Measurements were conducted at 25 °C under a constant shear strain of 1%, with frequency sweeps from 0.1 to 10 Hz. The tested gel composition consisted of 1 wt% copolymer, 0.6 wt% hydroquinone–hexamethylenetetramine (HQ–HMTA), and 0.05 wt% thiourea.

The microstructure of the copolymer gel (1 wt% copolymer) was examined by environmental scanning electron microscopy (ESEM). Samples were first freeze-dried for 24 h, mounted on copper stubs using conductive adhesive, and sputter-coated with gold prior to imaging to assess gel network integrity and thermal stability.

Thermogravimetric analysis (TGA) was employed to evaluate the thermal decomposition behavior of the gel. Measurements were performed from 30 °C to 600 °C at a heating rate of 12 °C·min^{−1} under nitrogen atmosphere.

Water-retention capacity of the gel was investigated via low-field nuclear magnetic resonance (NMR). The transverse relaxation time (T_2) distribution was analyzed to characterize the state and mobility of water within the gel network.

3. Results and Discussion

3.1. Effect of Copolymer Properties on Gelation Performance

Effect of copolymer types on gelation performance. The gelation performance of copolymer gel as a function of copolymer type is summarized in Table 1 and illustrated in Figure 3.

Table 1. Effect of copolymer type on the gelation performance (crosslinker concentration, 0.6%).

Copolymer Type	Monomer Ratio (AM to NVP or AMPS)	Copolymer Code	Copolymer Concentration (%)	Gelation Time (h)	Gel Strength/ Viscosity	Gel Strength After Aging	Dehydrate Rate (%)
P(AM/ NVP)	3:7	N37	1.0	16	E	D	0
			0.8	20	C	C	5
	4:6	N46	1.0	14	G	F	0
			0.8	18	F	F	3
	5:5	N55	1.0	12	H	H	0
			0.8	16	H	H	0
	6:4	N64	1.0	11	H	H	0
			0.8	14	H	H	0
	7:3	N73	1.0	9.5	H	H	0
			0.8	12	H	H	0
P(AM/ AMPS)	3:7	M37	1.0	-	5.36	-	-
			0.8	-	4.33	-	-
	4:6	M46	1.0	-	18.25	-	-
			0.8	-	15.32	-	-
	5:5	M55	1.0	-	31.61	-	-
			0.8	-	25.65	-	-
	6:4	M64	1.0	-	24.64	-	-
			0.8	-	20.12	-	-
	7:3	M73	1.0	-	21.43	-	-
			0.8	-	17.57	-	-

Note: “-” means not glued.

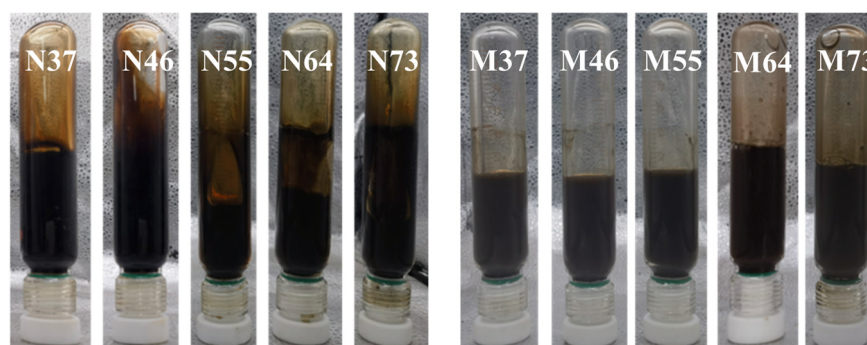


Figure 3. Effect of monomer ratio on the gelation performance of copolymers.

P(AM/AMPS) gel systems with varying monomer ratios and concentrations failed to form stable gels at 150 °C. During aging, the solution gradually darkened in color without a noticeable increase in system strength. After 24 h, the viscosity was measured and found to be substantially lower than the initial value. Black solid particles, presumably

resulting from high-temperature degradation of the copolymer, were also observed in the aged samples.

As shown in Figure 3, when using a polymer concentration of 1.0 wt% P(AM/NVP) as the base polymer and aging at 150 °C for 4 h, gel systems N46, N55, N64, and N73 all reached a Sydansk strength code of D. The viscosity increased markedly, with some gels adhering to the bottle wall and showing no flow upon inversion. System N37 exhibited a moderate increase in viscosity and was assigned a code of C, confirming that crosslinking occurred. The improved thermal stability likely stems from the more favorable influence of the NVP monomer compared with AMPS. The P(AM/NVP)-based systems maintained largely unchanged molecular weights before crosslinking and possess abundant amide groups that serve as crosslinking sites, enabling gels of tunable strength across different monomer ratios. Although the N37 gel system exhibited a shorter initial gelation time compared to other formulations, it displayed enhanced thermal resistance and better retention of amide groups at elevated temperatures. However, its absolute amide content remained lower than that of the other polymers investigated. The long-term stability of this system will be evaluated in future work.

The experiments shown in Figure 4 were performed using 1 wt% P(AM/NVP). After aging for 16 h, sample N37 reached a Sydansk code of E, forming a nearly immobile gel that largely adhered to the bottom and walls of the bottle. Following 6 months of aging, its strength declined to code D. Sample N46 initially exhibited code G, which decreased to code F after aging as the gel detached from the bottle bottom. Samples N55, N64, and N73 consistently maintained a code of H throughout the six-month period, with no significant change in gel strength.

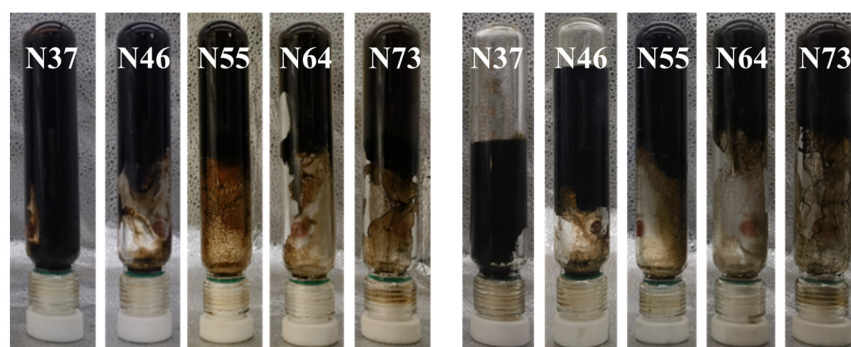


Figure 4. Effect of monomer ratio on the gel-forming properties of P(AM/NVP) copolymer systems ((left): after aging 16 h; (right): after aging 6 months).

Compared to systems prepared at 1.0 wt% copolymer, those formulated with 0.8 wt% N37 and N46 showed reduced gel strength and an extended gelation time of approximately 4 h. During long-term aging, these gels underwent mild syneresis, with dehydration rates of 5% and 3%, respectively, while their strength remained largely stable. For gels based on other monomer ratios, gelation time increased by 4–5 h, yet gel strength and overall structural integrity were well maintained, indicating good long-term stability.

Compared to the systems prepared with 1.0 wt% copolymer, those formulated at 0.8 wt% (N37 and N46) exhibited reduced gel strength and a gelation time prolonged by approximately 4 h. During long-term aging, mild syneresis was observed, with dehydration rates of 5% and 3%, respectively, while the gel strength remained largely stable. For systems with other monomer ratios, gelation time increased by 4–5 h, yet the resulting gels retained consistent strength and structural integrity, indicating good long-term stability. After 6 months of high-temperature aging, selected gel samples were retrieved for morphological examination (Figure 5). The gel maintained a continuous, elastic structure without visible

fracture or detachment from the supporting glass rod when gently shaken, confirming its retained integrity under prolonged thermal exposure.

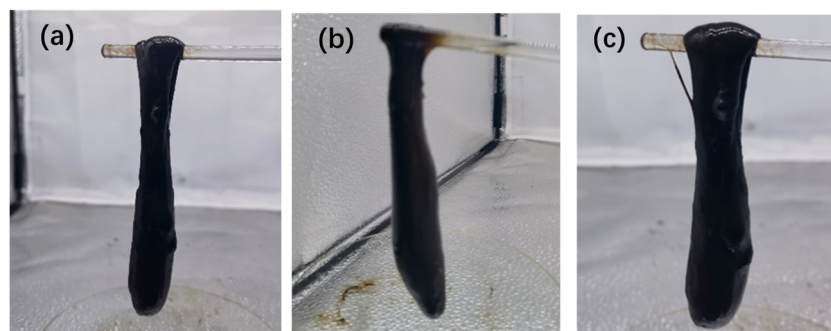


Figure 5. Morphology of P(AM/NVP) copolymer gels with varying monomer ratios after 6 months of aging at 150 °C ((a) N73; (b) N64; (c) N55).

Effect of copolymer molecular weight on gelation performance. The molecular weight of the copolymer significantly influences the performance of the gel-forming system. The molecular weights of the polymers were determined according to the literature. Each polymer powder was dissolved in an aqueous NaCl solution (58.5 g L^{−1}), and the intrinsic viscosity was measured using an Ubbelohde viscometer at 30 °C. The viscosity–average molecular weight (M_v) was then calculated via the Mark–Houwink–Sakurada equation [23]. The measured intrinsic viscosities and corresponding molecular weights are summarized in Table 2.

$$\eta_r = \frac{t}{t_0} \quad (1)$$

$$[\eta] = \frac{H}{c_0} \quad (2)$$

$$[\eta_{sp}] = \frac{(t - t_0)}{t_0} \quad (3)$$

$$[\eta] = 4.75 \times 10^{-3} M_v^{0.80} \quad (4)$$

where η_r is the relative viscosity; $[\eta]$ is intrinsic viscosity, mL/g; $[\eta_{sp}]$ is the specific viscosity; t is the flow time for polymer solution, s; t_0 is the flow time for 1.00 mol/L NaCl solution, s; c_0 is the concentration of polymer solution, mg/L; and M_v is the viscosity–average molecular weight, g/mol. By plotting $[\eta_{sp}]/c$ and $\ln [\eta_r]/c$ of polymer solution against concentration, extrapolating to infinite dilution, and taking the intercept, H is determined; if the intercept is not the same point, the average of the intercept is taken.

Table 2. Characteristic viscosities and relative molecular masses of copolymers at 25 °C.

Number	Mass Concentration of Initiator (%)	Viscosity (1 wt%, mPa·s)	Intrinsic Viscosity (mL/g)	Relative Molecular Mass (g/mol)
A	0.0625	124.3	874.7166	3,815,123
B	0.0750	89.36	666.0140	2,713,492
C	0.1000	59.29	475.8143	1,782,261

Gelation experiments were performed using copolymer solutions at two concentrations (0.8 wt% and 1.0 wt%) and three different molecular weights. The formulations contained HTMA (0.3 wt%) and HQ (0.3 wt%) as crosslinkers, and thiourea (0.05 wt%) as an oxygen scavenger. All solutions were prepared with deionized water. Gelation

performance was evaluated at 150 °C. The experimental results are summarized in Table 3 and illustrated in Figure 6.

Table 3. Influence of polymer molecular weight on the gelation performance.

Copolymer Number	Mass Concentration (%)	Crosslinker Concentration (%)	Gelation Time (h)	Gluing Strength	Strength After Aging and Water Precipitation Rate (%)	
C	1.0	0.60	18.5	F	E	5
	0.8		24	E	D	5
B	1.0		16	G	F	0
	0.8		20	F	F	3
A	1.0		14	G	F	0
	0.8		18	F	F	3



Figure 6. Gelation behavior of polymers with different molecular weights ((left): after aging 8 h; (right): after aging 6 h).

As summarized in Table 3, copolymers across a range of molecular weights successfully formed gels at 150 °C when crosslinked with HQ-HMTA. For illustration, results obtained at a copolymer concentration of 1.0 wt% are described below. A gel prepared with the highest-Mw copolymer ($3.82 \times 10^6 \text{ g mol}^{-1}$) reached a Sydansk code of G after only 14 h at high temperature, representing the shortest gelation time observed. After 6 months of aging, the gel strength decreased to code F, with no measurable syneresis. Using a copolymer of intermediate molecular weight ($2.71 \times 10^6 \text{ g mol}^{-1}$), the system attained code G after 16 h. Its strength later declined to code F during aging, though again no dehydration was detected over 6 months. These results suggest that within the tested Mw range ($2.71\text{--}3.82 \times 10^6 \text{ g mol}^{-1}$), lower molecular weight slightly delays gelation but does not compromise the ultimate gel strength or stability. In contrast, the lowest-Mw polymer ($1.78 \times 10^6 \text{ g mol}^{-1}$) reached code D within 8 h, peaked at code F after 18.5 h, and then settled at code E upon prolonged aging, accompanied by a syneresis rate of 5%.

At a copolymer concentration of 0.8 wt%, the resulting gel systems exhibited lower strength (Sydansk codes E to F) compared to those prepared at 1.0 wt%, along with a gelation time prolonged by 4–5.5 h. Following 6 months of aging, gels based on copolymers with molecular weights of 1.78×10^6 and $2.71 \times 10^6 \text{ g mol}^{-1}$ showed further decline in stability, with final strengths of code D and code F, respectively. Syneresis rates for these systems were measured at 5% and 3%.

3.2. Effect of Copolymer Properties on Modulus Strength

Effect of copolymer types on modulus strength. The rheological properties of selected gel samples were characterized after complete gelation. The corresponding storage (G') and loss (G'') moduli are presented in Figures 7 and 8.

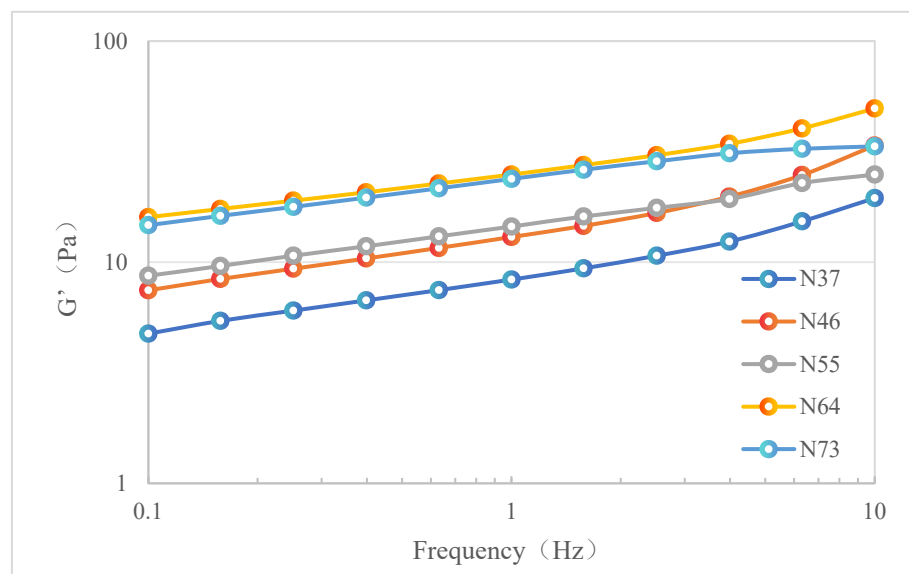


Figure 7. G' of gels formed from different copolymer types.

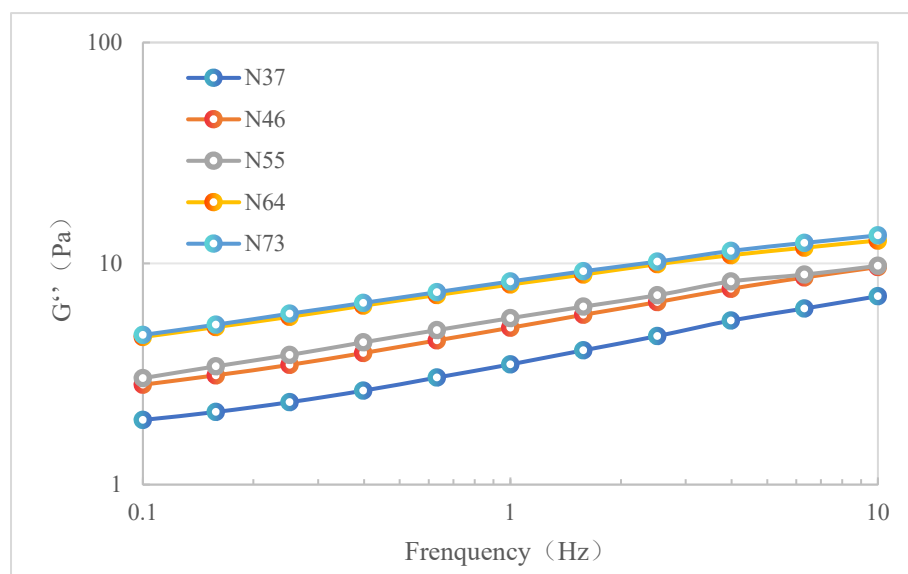


Figure 8. G'' of gels formed from different copolymer types.

The influence of monomer ratio in P(AM/NVP) copolymers on the G' of the corresponding gels is presented in Figure 6. Based on established criteria, gels are classified as strong ($G' > 10$ Pa), medium ($2 \leq G' \leq 10$ Pa), or weak ($G' < 2$ Pa) [24]. At a frequency of 0.1 Hz, the N64 and N73 systems exhibited G' values of 16.0 Pa and 14.7 Pa, respectively, corresponding to strong gels. In contrast, gels formed from N37, N46, and N55 displayed medium strength, with moduli of 8.68 Pa, 7.46 Pa, and 4.75 Pa. These results confirm that all tested formulations meet the typical mechanical thresholds required for field applications in oilfield conformance control.

Increasing the acrylamide (AM) content from 30 mol% to 60 mol% consistently enhanced the gel modulus, which is attributed to the higher density of available amide crosslinking sites. However, a further increase to 70 mol% (N73) led to an 8.1% reduction in G' compared to N64. This decrease may be explained by the higher susceptibility of the N73 copolymer to hydrolysis under the test conditions, resulting in a net loss of amide groups. The incorporation of N-vinylpyrrolidone (NVP) in the copolymer is known to

suppress amide hydrolysis, but its protective effect appears to be insufficient at very high AM contents [25,26].

The effect of monomer composition in P(AM/NVP) copolymers on the G'' of the gel systems is shown in Figure 8. At a shear frequency of 0.1 Hz, the G'' of the N37-based gel measured 1.96 Pa after high-temperature curing, which is below the typical threshold (>2 Pa) required for effective conformance-control gels in oilfield applications. In contrast, gels prepared with N46, N55, N64, and N73 exhibited progressively higher G'' values of 2.83 Pa, 3.03 Pa, 4.65 Pa, and 4.75 Pa, respectively, as the acrylamide content increased. The viscoelasticity of the gel, which directly reflects its strength, fundamentally determines mechanical stability and erosion resistance in porous media. Consequently, all four systems met the mechanical criteria for in-depth fluid diversion [25]. In addition, the gels maintained long-term stability with no observable syneresis after 6 months of aging.

Effect of copolymer molecular weight on modulus strength. The viscoelastic properties of gel systems prepared with copolymers of different molecular weights were further characterized using a high-temperature/high-pressure rheometer. All formulations contained 1.0 wt% copolymer, 0.6 wt% hydroquinone–hexamethylenetetramine (HQ–HMTA), and 0.05 wt% oxygen scavenger. The gels were cured at 150 °C prior to testing. The G' and G'' are presented in Figures 7 and 9, respectively.

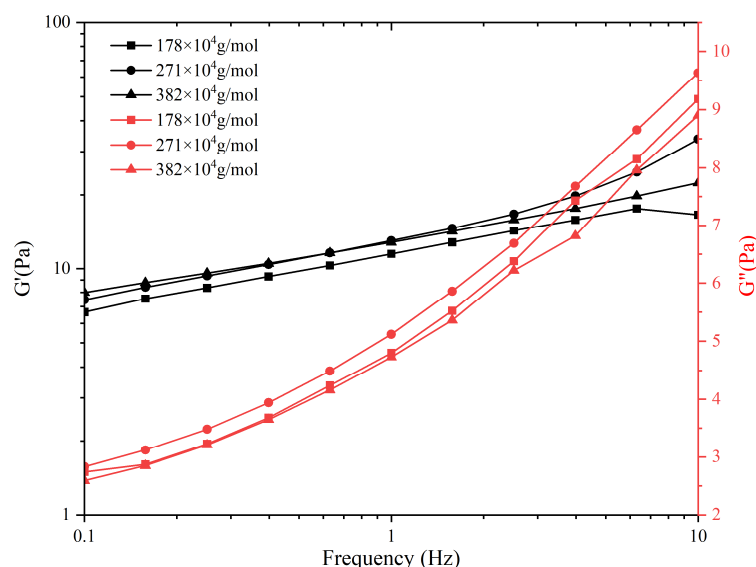


Figure 9. G' and G'' of gels formed from different copolymer weights.

The influence of copolymer molecular weight on the G' and G'' of the gel system is shown in Figure 9. At a frequency of 0.1 Hz, fully cured gels prepared from copolymers with molecular weights of 1.78×10^6 , 2.71×10^6 , and 3.82×10^6 g mol^{−1} exhibited G' values of $6.65(\pm 0.67)$ Pa, $6.99(\pm 0.70)$ Pa, and $7.46(\pm 0.75)$ Pa, respectively. The modest increase in G' with molecular weight indicates that gelation performance is only weakly dependent on Mw within this range. All three systems yielded gels of medium strength ($G' \approx 2$ –10 Pa), meeting the mechanical criteria required for conformance-control applications in reservoirs. The G'' -versus-frequency curves of the three systems nearly superimpose. At 0.1 Hz, gels prepared from copolymers with molecular weights of 1.78×10^6 , 2.71×10^6 , and 3.82×10^6 g mol^{−1} exhibited G'' values of $2.59(\pm 0.26)$ Pa, $2.74(\pm 0.27)$ Pa, and $2.83(\pm 0.28)$ Pa, respectively. In oilfield conformance-control applications, a G'' above 2 Pa is generally regarded as the threshold for effective gel performance. All systems tested here satisfy this criterion and are therefore mechanically suitable for in-depth water-shutoff operations.

3.3. Effect of Copolymer Properties on Gel Microstructure

Effect of copolymer types on gel microstructure. The microstructure of gels formed from P(AM/NVP) copolymers with five different monomer ratios is presented in Figure 10. All gels exhibit a stable, continuous microstructure characterized by an interconnected network with both reticular and lamellar features, and no macroscopic fractures are observed. When the acrylamide content exceeds 50 mol%, the gel network becomes notably more compact, displaying finer mesh sizes and a higher proportion of sheet-like domains. This densified microstructure enhances the gel's ability to retain water, which in turn contributes to its improved mechanical strength.

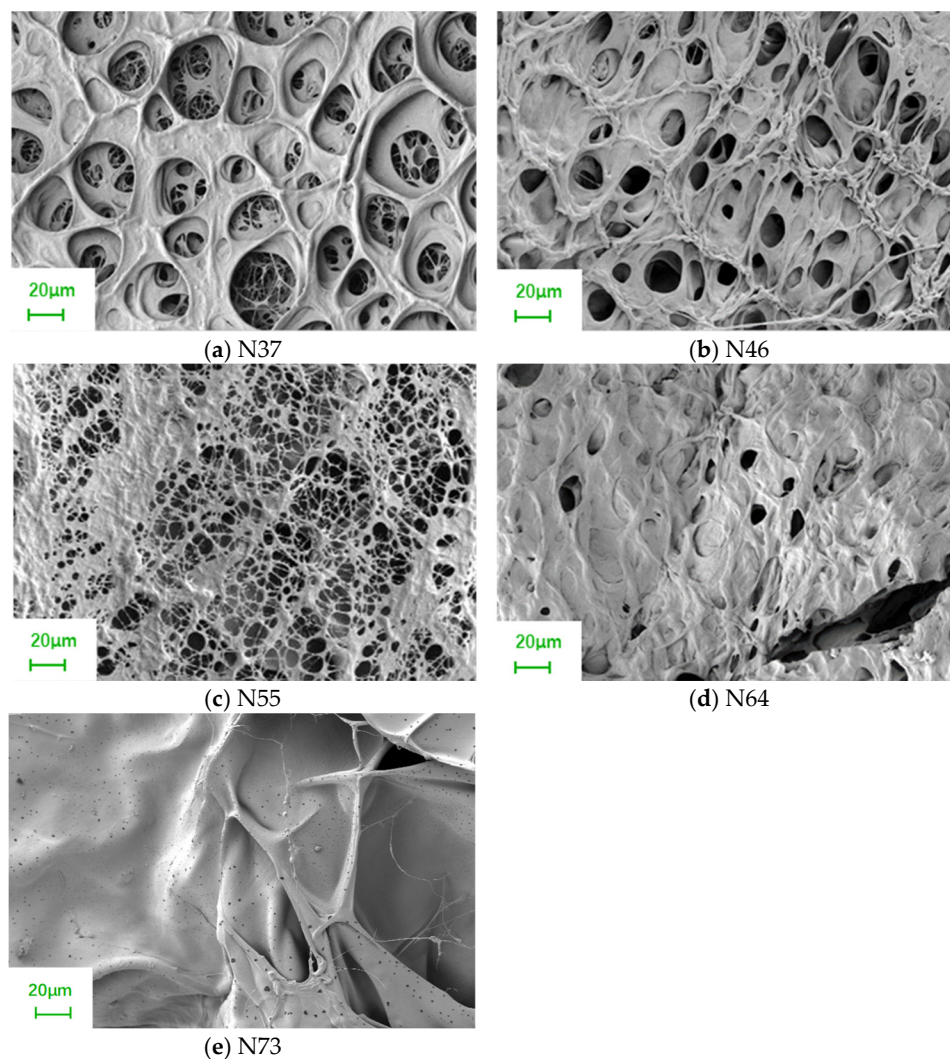


Figure 10. Microstructure of gels prepared from different copolymer types.

Representative microstructures of gels formed from N37, N46, and N55 were examined at higher magnification to quantify the network mesh size, as displayed in Figure 11. The measured mesh sizes ranged from 25.75 μm to 33.96 μm for N37, 17.75 μm to 26.71 μm for N46, and 2.62 μm to 3.13 μm for N55. These results demonstrate a pronounced reduction in mesh size with increasing acrylamide (AM) content.

Rheological measurements further indicate that gels with smaller mesh sizes consistently exhibit higher G' and G'' moduli. This trend is attributed to the greater density of crosslinking sites available at higher AM contents, which promotes the formation of a more compact network. In the case of N64 and N73 gels—which possess the highest AM contents—the microstructure transitions toward a more lamellar morphology, contributing

to their superior mechanical strength compared to the predominantly reticular networks of N37, N46, and N55.

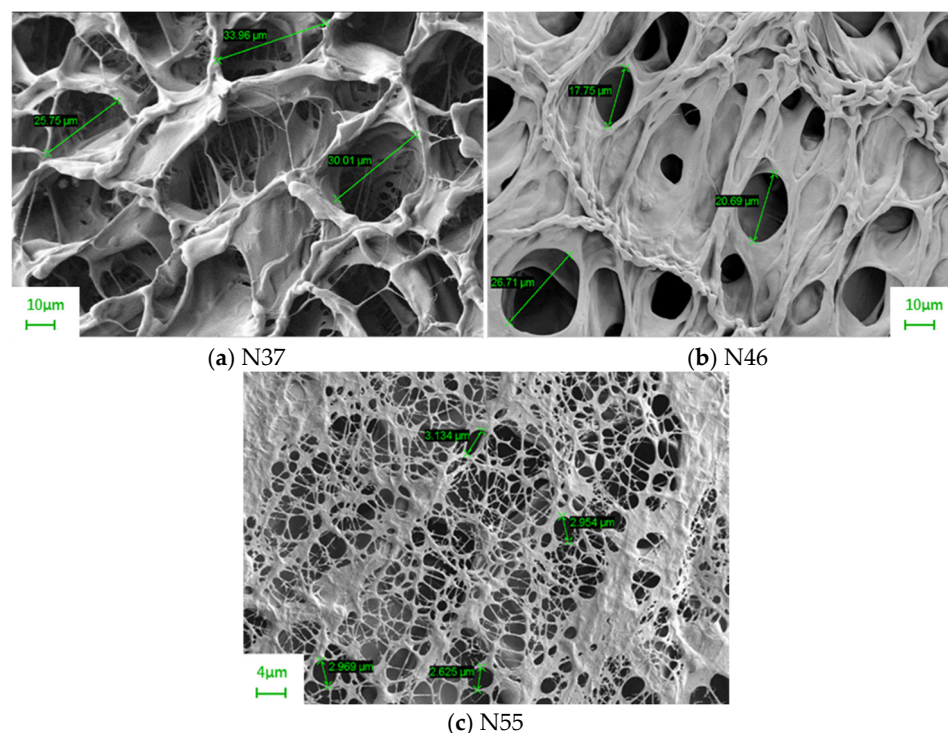


Figure 11. Microscopic mesh size of gels prepared from different copolymer types.

Effect of copolymer molecular weight on gel microstructure. Increasing the molecular weight of the copolymers led to consistent improvements in the gelation behavior: shorter gelation times, higher gel strength, and enhanced long-term stability without observable syneresis. To correlate these macroscopic properties with structural features, the microstructures of gels prepared from polymers with molecular weights of 1.78×10^6 and $2.71 \times 10^6 \text{ g mol}^{-1}$ were examined (Figure 12a). For comparison, the microstructure of the gel formed with the highest-Mw polymer ($3.82 \times 10^6 \text{ g mol}^{-1}$) is presented in Figure 12b. These images confirm that higher molecular weight promotes a more robust and stable gel network.

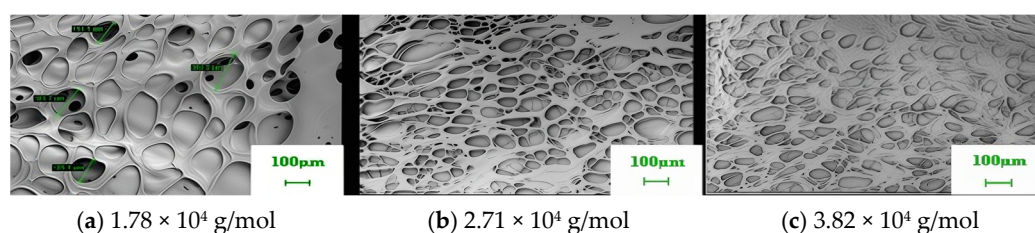


Figure 12. Microstructure of gels prepared from different copolymer molecular weights.

At higher molecular weights, the gel network exhibits a marked increase in mesh density and a corresponding reduction in average mesh size. For the gel prepared with the lowest-Mw polymer, the mesh sizes are broadly distributed between 125.1 μm and 203.2 μm . As the molecular weight rises to 2.71×10^6 and $3.82 \times 10^6 \text{ g mol}^{-1}$, the number of discernible meshes within the same field of view increases substantially, with mesh sizes converging around 100 μm . This trend indicates that longer polymer chains facilitate the formation of a denser, more interconnected three-dimensional network, which

directly contributes to the improved mechanical and stability properties observed at higher molecular weights.

3.4. Influence of Polymer Properties on Gel Thermal Stability and Governing Mechanisms

Effect of copolymer types on thermal stability. The thermal degradation behavior of the different gel systems was characterized by TGA, as shown in Figure 13. The mass-loss process occurs in three distinct stages. The first stage, below ~ 150 °C, is attributed to the evaporation of physically and hydrogen-bonded water, with the extent of loss depending on the initial water content of the gel. The second stage, between approximately 150 °C and 300 °C, corresponds to the decomposition of the crosslinked network and the onset of carbonization. The third stage, from about 350 °C to 500 °C, involves the breakdown of the polymer backbone and side chains, leading to further carbonization and ultimately to residual ash.

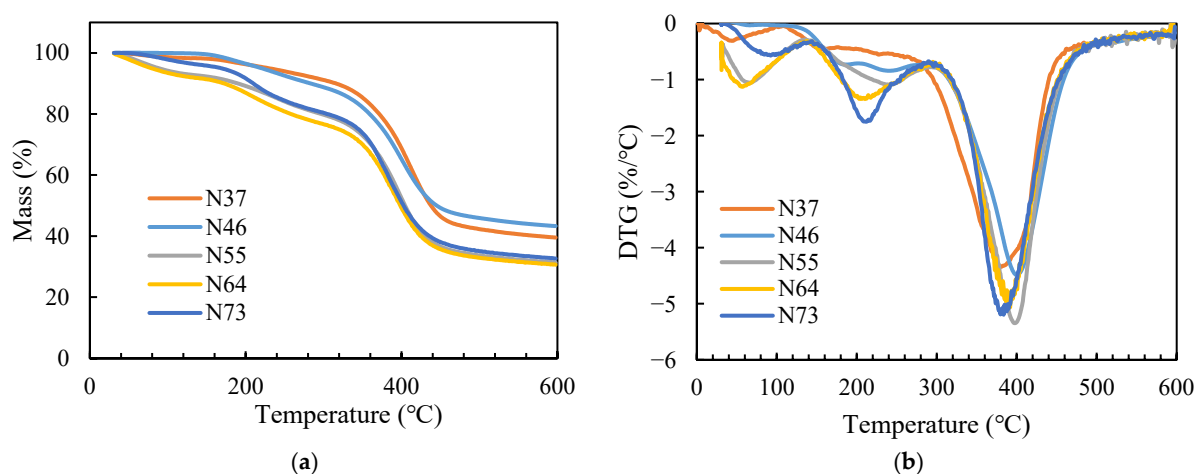


Figure 13. TG and DTG curves of P(AM/NVP) with different monomer contents.

For direct comparison, the absolute peak intensities of the second and third derivative thermogravimetry (DTG) peaks and their corresponding temperatures are presented as bar charts in Figure 14. The data indicate that gels with lower NVP content exhibit more pronounced derivative DTG peaks during the second degradation stage, reflecting a higher rate of mass loss. Concurrently, the temperature at which the DTG peak occurs shifts to lower values as the proportion of thermally labile monomers increases, suggesting reduced stability of the crosslinked network. Despite this trend, all observed DTG peak temperatures exceeded 212 °C, which implies that the crosslinked structures remain sufficiently stable to resist thermal breakdown under the target application condition of 150 °C. In addition, the apparent divergence in chemical thermal stability (as measured by TGA) and macroscopic long-term stability observed in high-molecular-weight polymers originates from fundamentally different governing mechanisms at the molecular versus macroscopic scales. At the chemical level, increased molecular weight, which corresponds to longer primary chains, can sterically hinder complete crosslinking. The resulting network imperfections—such as unreacted sites or low-crosslink-density regions—act as weak points that preferentially initiate chain-scission degradation upon heating, thereby lowering the onset temperature in thermogravimetric analysis. In contrast, macroscopic long-term stability is governed primarily by physical topology. High molecular weight drastically increases entanglement density, creating a pervasive physical network that severely constrains chain segment mobility. This topological constraint effectively impedes large-scale flow, creep, and permanent deformation, thereby conferring superior long-term dimensional and mechanical stability.

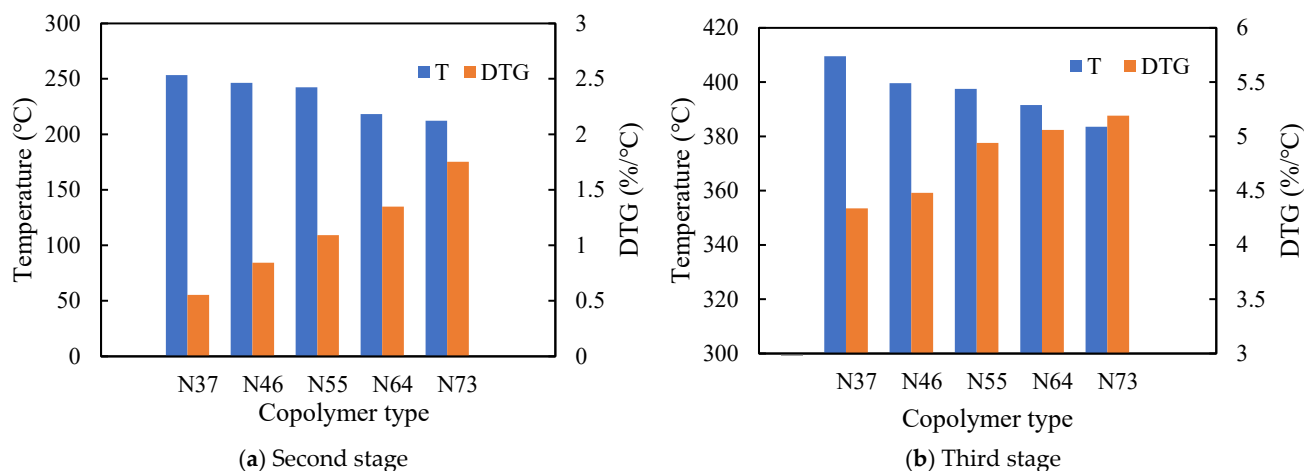


Figure 14. Relationship between DTG peak temperatures and intensities for different gel systems across degradation stages.

In summary, the thermal stability of the gel systems and the integrity of their crosslinked networks are positively correlated with the content of thermally stable comonomers in the copolymer backbone. This enhancement can be attributed to the presence of pyrrolidone rings in the NVP units, which dissipate thermal energy through molecular vibration, thereby mitigating the risk of decomposition in adjacent structural units. This observation is consistent with the findings reported by Ge et al. [16], who noted that after 6 months of aging at 155 °C, P(AM/AMPS/NVP) gels exhibited syneresis, yet signals corresponding to pyrrolidone rings remained detectable via ^{13}C NMR. Concurrently, substantial hydrolysis of amide and AMPS side groups led to a pronounced attenuation of their spectral signals. However, gelation experiments in this study indicate that an excessively high NVP content, as exemplified by the N37 formulation, can result in measurable syneresis after extended aging. This suggests that beyond an optimal threshold, high NVP content may compromise the water-retention capacity of the gel network.

Effect of copolymer types on NMR T_2 spectra. The T_2 distributions for the different gel systems are presented in Figure 15. In general, a shorter T_2 value at the signal peak reflects stronger binding of water within the gel network. This binding arises from two primary mechanisms: physical confinement of water molecules within the three-dimensional polymer matrix, and chemical hydration mediated by functional groups of the polymer. For clear comparison, the peak T_2 values of each system are summarized in the bar chart shown in Figure 16.

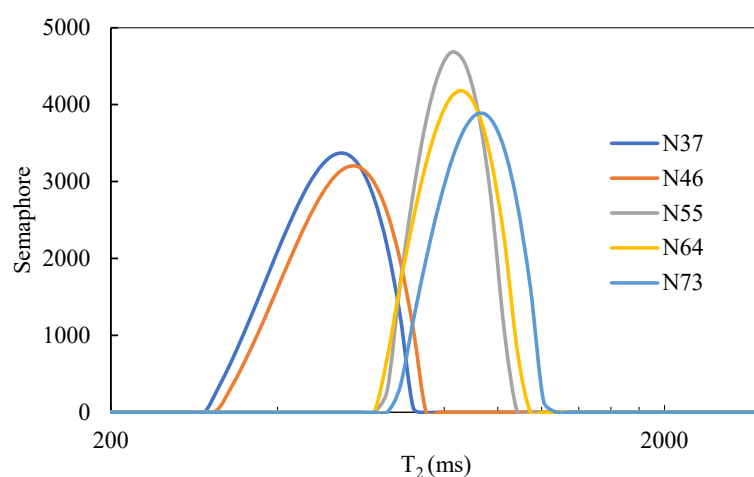


Figure 15. T_2 spectra of gel formed with copolymers of different monomer ratios.

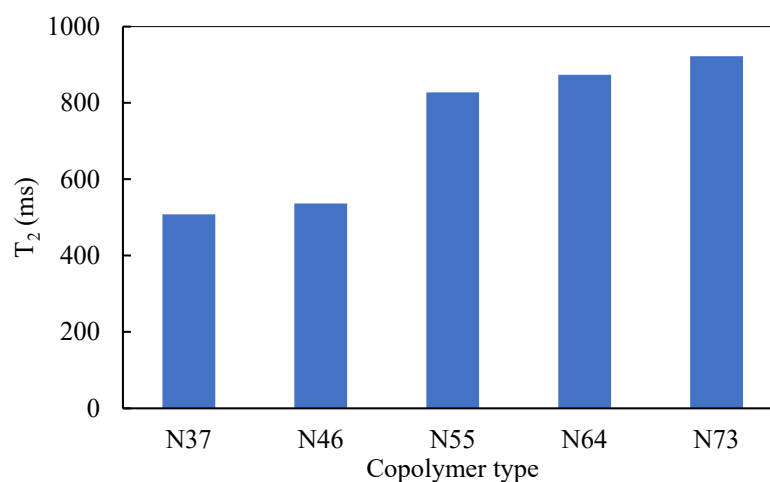


Figure 16. T_2 values corresponding to the peak signals of gel formed with copolymers of different monomer ratios.

As shown in Figure 16, the peak T_2 values of the gel systems increase with higher NVP content. Specifically, T_2 rises from 508 ms at 30 mol% NVP to 536 ms at 40 mol% NVP, representing a modest increment. A more pronounced increase is observed at 50 mol% NVP, where T_2 reaches 827 ms; further increases in NVP content result in only marginal additional rises. These trends indicate that gels with lower NVP content exhibit weaker water-binding capacity. This behavior can be attributed to the superior hydration ability of the pyrrolidone ring compared to conventional amide groups. The high hydrogen-bonding propensity of NVP enhances the overall hydration of the polymer, thereby strengthening its interaction with water molecules in the gel network.

Effect of copolymer molecular weight on thermal stability. Gel systems prepared with copolymers of different molecular weights, all at a fixed concentration of 1.0 wt%, were selected for thermogravimetric analysis. The resulting TG and DTG curves are shown in Figure 17. For direct comparison, the absolute peak intensities of the second and third DTG stages and their corresponding temperatures are summarized in the bar chart presented in Figure 18.

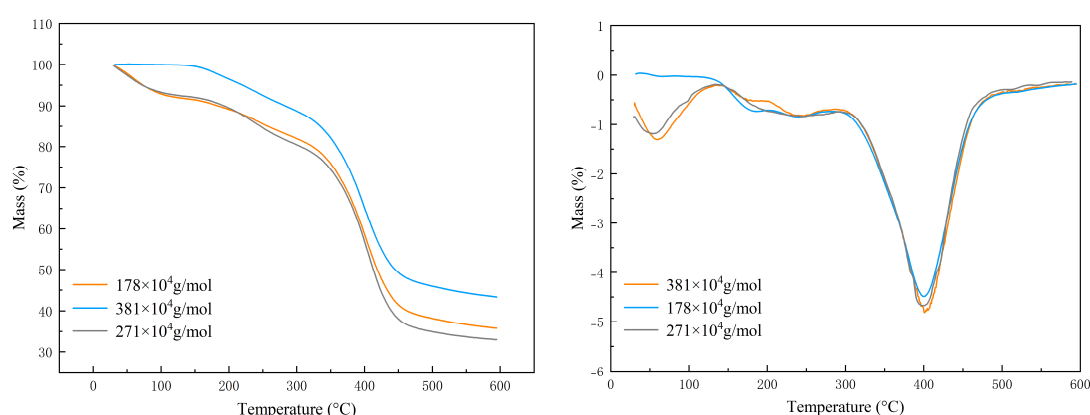


Figure 17. TG and DTG curves of P(AM/NVP) with different molecular weights.

As shown in Figure 18a, during the second degradation stage, the peak intensity of the DTG curve remains largely unchanged with increasing molecular weight. However, the corresponding peak temperature decreases systematically, indicating a gradual decline in the thermal stability of the crosslinked network. In the third degradation stage (Figure 18b), the DTG peak temperature remains relatively constant across different molecular weights, yet the peak intensity rises significantly. This increase reflects a greater extent of mass

loss, suggesting that the chemical structure of the gel network becomes progressively less resistant to thermal decomposition at higher temperatures.

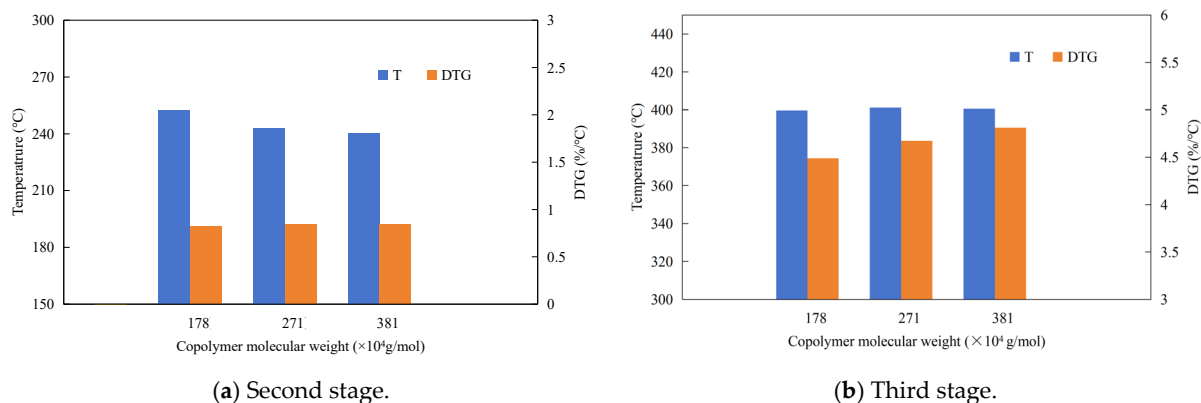


Figure 18. Relationship between DTG peak temperatures and intensities for different gel systems across degradation stages.

Effect of copolymer molecular weight on NMR T_2 spectra. Subsequently, fully cured gel systems with different compositions were analyzed at room temperature using low-field nuclear magnetic resonance (NMR). The corresponding T_2 distributions are presented in Figures 19 and 20. The peak T_2 values—536.3 ms, 597.7 ms, and 742.3 ms correspond to decreasing polymer molecular weights. This trend indicates that gels prepared from higher-Mw polymers exhibit shorter T_2 relaxation times, reflecting stronger water-binding affinity. The underlying mechanism may involve the more coiled conformation of longer copolymer chains in solution, which promotes hydration. Upon crosslinking, these chains form a denser network with finer pores, thereby enhancing physical confinement and binding of water molecules.

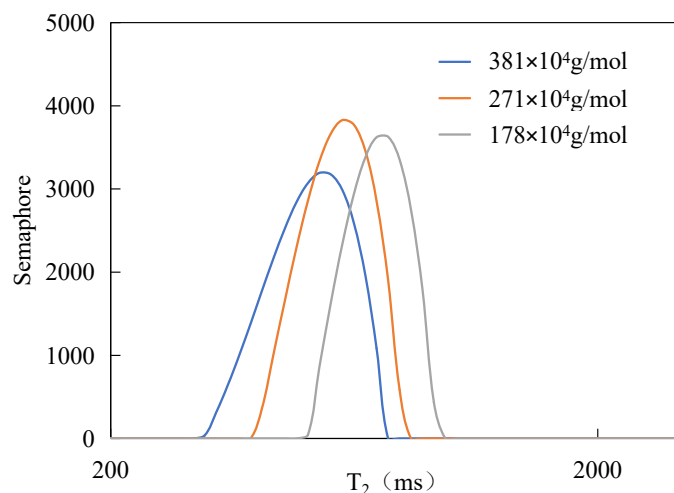


Figure 19. T_2 NMR spectra of gel systems prepared from polymers of different molecular weights.

A comprehensive analysis integrating gelation behavior, rheological moduli, microstructure, thermogravimetry, and T_2 distributions reveals that while higher Mw slightly reduces the chemical stability of the gel network under thermal degradation, it significantly improves water-retention capacity. Notably, variations in gel strength—both cohesive and elastic—remain within a moderate range, and all systems maintain a medium-strength profile. Nevertheless, higher Mw leads to shorter gelation times and enhanced long-term stability without syneresis. Within the studied molecular-weight range, all polymers

satisfy the basic mechanical and stability requirements for conformance-control applications in reservoirs. To achieve further strength enhancement, modifying the copolymer composition—particularly by increasing acrylamide content—could be considered.

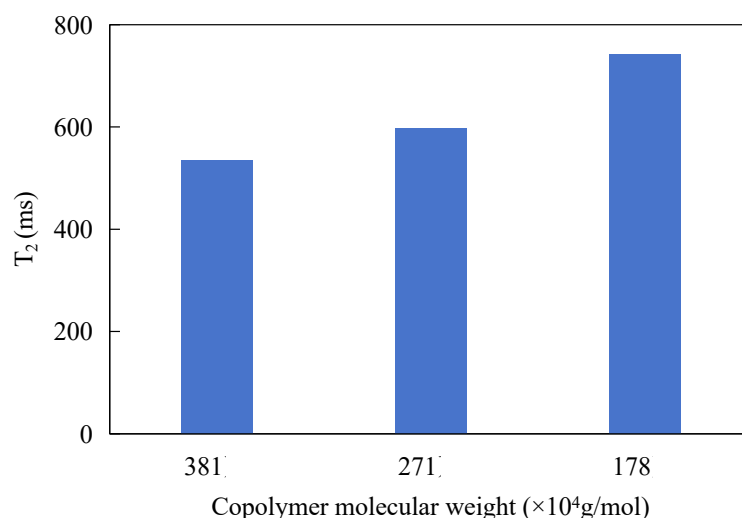


Figure 20. T_2 values corresponding to the signal peaks of gel systems prepared from polymers of different molecular weights.

4. Conclusions

This study systematically investigates the gelation behavior of different polymers and molecular weights at 150 °C, employing a multi-method approach that includes visual gel-code evaluation, rheological measurements, microstructural imaging, TGA, and low-field NMR. The principal conclusions are summarized as follows:

- (1) The gelation performance is strongly influenced by the type and content of thermally stable monomers in the copolymer. P(AM/NVP) exhibits excellent gel-forming capability under high-temperature conditions, whereas P(AM/AMPS) fails to form a stable gel, indicating insufficient intrinsic thermal resistance and the need for further structural modification.
- (2) Increasing the NVP content in P(AM/NVP) prolongs gelation time and reduces gel strength, but enhances the chemical stability and water-retention capacity of the resulting gel. Microstructurally, higher NVP content leads to a more open network, which can compromise long-term integrity. An optimal NVP content of 30–40 mol% combined with a polymer concentration of 1.0 wt% delivers the most balanced performance: gelation time of 9.5–11 h, G' of 14.7(± 0.15)–16.0(± 1.6) Pa, G'' of 4.65(± 0.47)–4.75(± 0.48) Pa, and stable gel morphology for over six months at 150 °C—meeting the requirements for conformance control in high-temperature reservoirs.
- (3) Increasing the polymer molecular weight from 1.78×10^6 to 3.82×10^6 g mol^{−1} shortens gelation time from 18.5 h to 14 h and improves the Sydansk gel-code from F to G, while the viscoelastic moduli remain within a narrow range ($G' = 6.65$ –7.46 Pa; $G'' = 2.74(\pm 0.27)$ –2.83(± 0.28) Pa). Microstructurally, higher molecular weight yields a denser network with smaller pore sizes, which enhances water binding but slightly reduces the thermal stability of the chemical network. Despite this trade-off, all systems in this molecular-weight range satisfy the essential criteria for field application.

Author Contributions: Methodology, Z.Y., J.B., Y.L., M.L., B.C. and J.C.; validation, Z.Y., J.B., Y.L., M.L. and B.C.; investigation, Z.Y., J.B., Y.L., M.L., B.C. and J.C.; writing—original draft, J.C.; visualization, Z.Y., J.B., Y.L., M.L. and B.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (Grant No. 52304043).

Institutional Review Board Statement: Not applicable.

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Acknowledgments: The authors acknowledge the financial support generously provided by the National Natural Science Foundation of China (Grant No. 52304043) for this study.

Conflicts of Interest: Author Zhande Yang, Jing Bai, Yanheng Liang, and Mengyu Liu were employed by the Xi'an ChangQing Chemical Group Co. Ltd., and author Bowen Chen was employed by the Shale Gas Research Institute of PetroChina Southwest Oil & Gas Field Company. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as potential conflicts of interest.

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