

Preparation and characterization of poly(NIPAAm-co-AMPS-co-Fe(phen)₃) self-oscillating copolymers

Jie Ren^{1,2} · Li Tao¹ · Guangcheng Zhang² · Mengqi Yao¹ · Jinfen Gu¹ · Wu Yang¹

Received: 12 August 2015 / Revised: 29 February 2016 / Accepted: 9 March 2016 / Published online: 22 March 2016
© Springer-Verlag Berlin Heidelberg 2016

Abstract A novel self-oscillating copolymer was prepared by utilizing Fe(phen)₃ as the catalyst of the Belousov–Zhabotinsky (BZ) reaction. In this study, 2-acrylamido-2-methylpropane sulfonic acid (AMPS) was newly introduced into the copolymer of *N*-isopropylacrylamide (NIPAAm) and Fe(phen)₃ as the H⁺ providing agent for the BZ reaction. The results indicated that the copolymer solution underwent soluble–insoluble self-oscillation only in malonic acid (MA) and potassium bromate (KBrO₃) mixture solution, and the amplitudes were much bigger than those of poly(NIPAAm-co-Fe(phen)₃). That is to say, the novel copolymer succeeds in self-oscillating under acid-free conditions. Moreover, the oscillating characteristics were closely related to the content of AMPS in the copolymer.

Keywords Self-oscillating copolymer · Poly(NIPAAm-co-AMPS-co-Fe(phen)₃) · BZ reaction

Introduction

Since the first report [1] about self-oscillating polymers or gels (SOPs) which can exhibit spontaneous changes with temporal or spatiotemporal periodicity without applying any on–off switching of external stimuli, many types of SOPs that undergo soluble–insoluble or swelling–deswelling changes have been developed by Yoshida et al. [2–5]. In general, such systems are constructed by coupling responsive components with chemical oscillators. The chemical oscillators serve as the periodical driving source which exhibit autonomous, reversible, and periodical change in some factors such as pH value, redox potential, concentrations of intermediates, and so on. The responsive components can respond timely and reversibly to the periodical variation of the oscillating factors generated in the chemical oscillating reaction and exhibit self-oscillating behaviors.

For a typical SOP system explored by Yoshida et al., the Belousov–Zhabotinsky (BZ) reaction is exploited as the driving source for the similarity with the tricarboxylic acid (TCA) cycle, a key metabolic process that takes place in living bodies, and the chemical model for understanding several autonomous phenomena in biological systems and NIPAAm as the responsive component. The overall process of BZ reaction is the oxidation of an organic substrate by an oxidizing agent in the presence of a metal ion or metal complex catalyst with high redox potentials, such as cerium ion, ferroin, or ruthenium tris(2,2′-bipyridine) (Ru(bpy)₃²⁺) under acidic conditions [6]. While the reaction proceeds, the catalyst undergoes spontaneous redox oscillation. The BZ catalyst is firstly modified with double bond and then copolymerized with the responsive components by covalently bonds (often Ru(bpy)₃²⁺ was used) which bridge the BZ reaction and the polymer systems. Generally, the hydrophilicity of the polymer chains increases in the oxidized Ru(III) state and decreases in the reduced

✉ Jie Ren
Jieren@nwnu.edu.cn

¹ Chemistry & Chemical Engineering College, Key Lab of Bioelectrochemistry & Environmental Analysis of Gansu, Northwest Normal University, Lanzhou 730070, People's Republic of China

² School of Natural and Applied Science, Northwestern Polytechnical University, Xi'an 710072, People's Republic of China

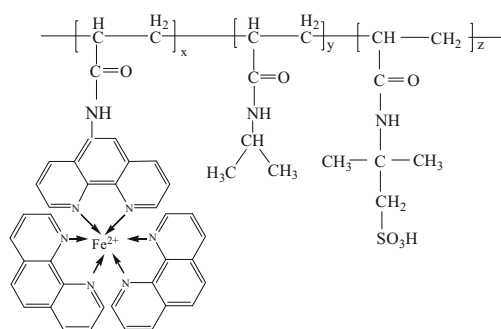


Fig. 1 The chemical structure of the self-oscillating copolymer chain

Ru(II) state. Due to the redox oscillation of $\text{Ru}(\text{bpy})_3$, the polymer chains undergo spontaneous soluble–insoluble transition or swelling–deswelling (for gels) oscillation with the redox oscillation in the closed solution under constant conditions.

The traditional SOPs are often composed of a metal catalyst for the BZ reaction and other responsive components. And most of them are the copolymers of NIPAAm and $\text{Ru}(\text{bpy})_3$ moiety. Therefore, design of new self-oscillating polymers with unique chemical structures and excellent performances can be performed as the following two aspects. One way is copolymerization of other functional components with $\text{Ru}(\text{bpy})_3$. Several new SOPs have been studied by introduction of other components, such as 2-acrylamido-2-methylpropane sulfonic acid (AMPS), methacrylamidopropyltrimethylammonium chloride (MAPTAC), acrylic acid (AA), N-Acryloxysuccinimide (NAS), poly(vinylpyrrolidone) (PVP), spirobenzopyran, etc. [3, 7–13]. The solubility of the NIPAAm-*co*-AMPS-*co*- $\text{Ru}(\text{bpy})_3$ copolymer chains is more than that of NIPAAm-*co*- $\text{Ru}(\text{bpy})_3$, and the soluble–insoluble self-oscillation can be realized in an acid-free condition [7]. When the copolymer hydrogel is prepared, a phase-separated structure is obtained and the amplitude of volume self-oscillation of the hydrogel is improved significantly [8]. Introduction of MAPTAC enables the self-oscillation behavior under oxidant-free conditions for the strong oxidation ability [9]. By introducing both AMPS and MAPTAC, self-oscillation of the copolymer in only MA solution can be realized, just like fuel-driven machines [10]. More interesting, when AA is

introduced, the occurrence and stop of self-oscillating behaviors can be controlled by temperature [3]. Spirobenzopyran was also introduced into the poly(NIPAAm-*co*- $\text{Ru}(\text{bpy})_3$) [11] as a photochromic site, and the copolymer solution shifts to a lower temperature with isomerization from McH to spirobenzopyran by photoirradiation. Therefore, photo-regulation of the self-oscillating motion of the gel was experimentally demonstrated.

The other way is exploration of new BZ catalysts. Except for $\text{Ru}(\text{bpy})_3$, many other metal ions or their complexes can also serve as the BZ catalysts, such as Ce^{4+} , Mn^{2+} , $\text{Fe}(\text{phen})_3^{2+}$, $\text{Fe}(\text{bpy})_3$, and so on. Some of them have been recently exploited for the design of SOPs. Hara et al. [14, 15] demonstrated that $\text{Ru}(\text{bpy})_3$ catalyst could be substituted by $\text{Fe}(\text{bpy})_3$. Although the utilization of iron greatly lowers the cost for preparing the BZ reaction catalyst, the soluble–insoluble self-oscillating amplitude is smaller than that of $\text{Ru}(\text{bpy})_3$ -based copolymer. Another typical example is presented by the self-oscillating gel actuator driven by ferroin. We modified 1,10-phenanthroline with a double bond and obtained iron(5-acrylamido-1,10-phenanthroline) bis(1,10-phenanthroline) (for simplicity, it is abbreviated as $\text{Fe}(\text{phen})_3$) monomer and then copolymerized with NIPAAm to get the linear copolymer [16]. Both the redox potential and transmittance oscillate spontaneously in homogeneous system. Arimura et al. [17] also obtained poly(NIPAAm-*co*- $\text{Fe}(\text{phen})_3$) gel. When the gel is immersed into the BZ reaction solution, a redox oscillation of ferroin can be observed and the gel can exhibit 7 % swelling/deswelling variation in the gel length.

The self-oscillating mechanisms involving $\text{Ru}(\text{bpy})_3$, $\text{Fe}(\text{bpy})_3$, and $\text{Fe}(\text{phen})_3$ copolymers or gels are based on the hydrophilic/hydrophobic transition of BZ catalyst moieties. Different from these systems, the coupling of $\text{Ru}(\text{II})(\text{tpy})_2$ and the BZ reaction has been paid much attention as it provides a new approach to autonomous viscosity oscillation by dynamic interaction upon redox stimuli [18, 19]. When the Ru ion is in the oxidized Ru(III) state, it forms a mono-complex ($\text{Ru}(\text{tpy})_3^{3+}$) with a single terpyridine ligand, while in the reduced Ru(II) state, it forms a biscomplex ($\text{Ru}(\text{tpy})_2^{2+}$). Although the amplitude of viscosity oscillation in this experiment is still small for practical applications, larger amplitude can be expected by control of the molecular weight.

Table 1 The amounts of reactants in each prepared copolymer

Samples	NIPAAm (g)	AMPS (g)	5-AM-phen (g)	AIBN (g)	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (g)	phen (g)
P100-0	5.0	0	0.2	0.01	0.21	0.4
P90-10	4.5	0.5	0.2	0.01	0.21	0.4
P50-50	2.5	2.5	0.2	0.01	0.21	0.4
P20-80	1.0	4.0	0.2	0.01	0.21	0.4

It was demonstrated that the $\text{Fe}(\text{phen})_3$ moiety could be employed as the metal catalyst in the BZ reaction. However, the amplitudes both of the soluble–insoluble oscillation for linear copolymer and the swelling–deswelling change for gel were still smaller than $\text{Ru}(\text{bpy})_3$ -based ones. In the present study, AMPS was introduced into the copolymer chain and several copolymers were prepared containing different AMPS. The autonomous redox potential and absorbance oscillations derived from the hydrophilic/hydrophobic transition of copolymer chains coupled with the BZ reaction were investigated.

Experimental

Materials

N-isopropylacrylamide (NIPAAm), azo-bis-isobutyronitrile (AIBN), and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) were brought from Shanghai Zhongqin Chemical Industry and used without further purification. Ethanol, dichloromethane, and methanol (Tianjin Guangfu Fine Chemical Industry Research institute, Tianjin, China) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, malonic acid (MA), KBrO_3 , H_2SO_4 , $\text{Ce}_2(\text{SO}_4)_3$, and $\text{Ce}(\text{SO}_4)_2$ were used. All the reagents mentioned above were analytical reagents and used as received. 5-acrylamido-phenanthroline (5-AM-phen) was synthesized by us. The deionized water was used throughout the experiments.

Preparation of poly(NIPAAm-co-AMPS-co- $\text{Fe}(\text{phen})_3$)

The self-oscillating copolymers (Fig. 1) with different compositions were synthesized as follows: 5-AM-phen(0.20 g), NIPAAm, and AMPS (total 5.0 g, their ratios are listed in Table 1) were dissolved in ethanol (25 g). The mixture was poured into a 250 mL three-neck, round-bottom flask equipped with a stirrer, a condenser, and a nitrogen gas inlet. The copolymerization reaction was performed at 80 °C for 6 h under N_2 bubbling. The obtained copolymer (0.10 g) was dissolved in dichloromethane, and the solution of $\text{Fe}(\text{II})$ in methanol was added dropwise with stirring at room temperature for 30 min. Finally, the solution of phenanthroline in ethanol was added dropwise with stirring at room temperature for 1 h. The resultant sample was dialyzed with ethanol for 2 months while changing ethanol frequently, and then dialyzed with water for 2 weeks by daily changes of water. Finally, the sample was freeze-dried.

Characterization

FT-IR spectroscopy The samples were dried at 60 °C under vacuum for FT-IR measurement. The FT-IR spectroscopy was obtained on a Model FTS-3000 spectrometer

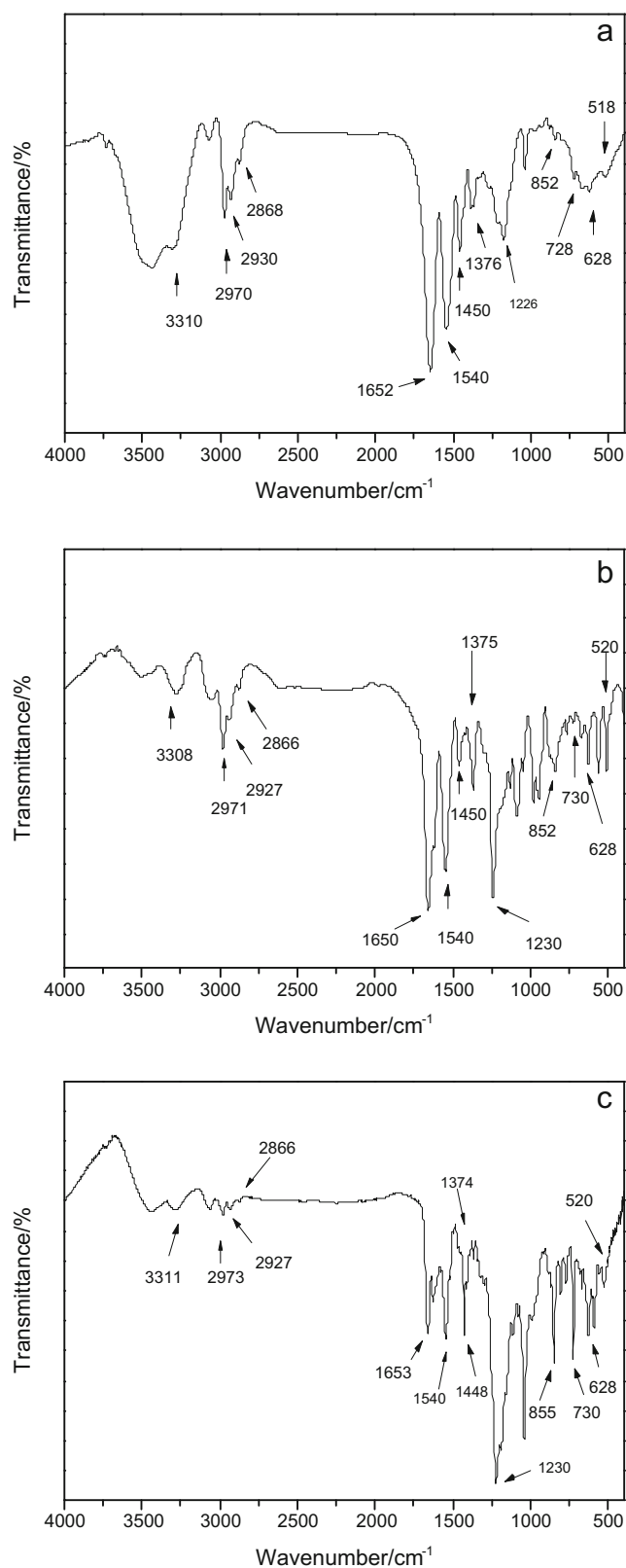


Fig. 2 The FT-IR spectra of the prepared copolymers (a P90-10, b P50-50, c P20-80)

(DIGILABGON, USA) and recorded over the range of 500–4000 cm^{-1} by KBr pellet method.

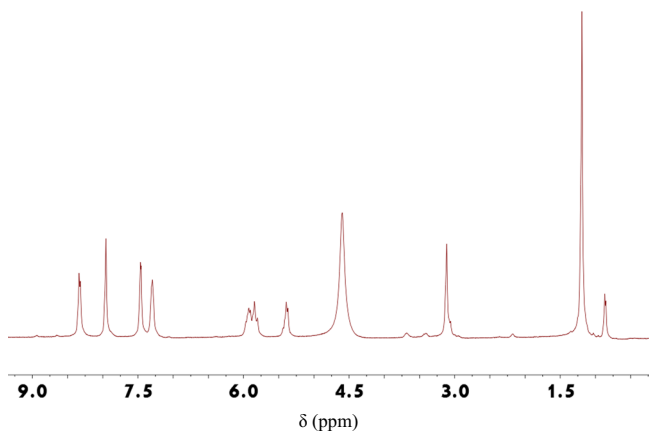


Fig. 3 The ^1H NMR spectra of prepared copolymers

^1H NMR spectroscopy The samples were dried at $60\text{ }^\circ\text{C}$ under vacuum. ^1H NMR spectroscopy was recorded on a Varian Mercury plus 400 spectrometer at room temperature ($20\text{ }^\circ\text{C}$). D_2O was used as the solvent for ^1H NMR measurement.

X-ray photoelectron spectroscopy X-ray photoelectron spectroscopy (XPS) measurements were performed by ESCALAB 250Xi (Thermo Fisher Scientific).

Measurement of the isosbestic point

Solutions of poly(NIPAAm-*co*-AMPS-*co*-Fe(phen) $_3$) (0.4 wt%) were prepared by dissolving the copolymers in deionized water. Reduced and oxidized copolymer solutions were prepared by adding 4 mM $\text{Ce}_2(\text{SO}_4)_3$ and 4 mM $\text{Ce}(\text{SO}_4)_2$, respectively. The isosbestic point measurements were carried out using a UV-Vis spectrophotometer (Beijing Puxi Co., Ltd., China, Model TU-1901) equipped with a thermostatic controller. The results indicated that isosbestic points of the three prepared copolymers were 400 nm.

Measurement of potential self-oscillation

The experiments were performed in a glass reactor (ca. 50 mL) coupled with a SY-601 thermostat and a Model ML-902 magnetic stirrer. A mixture containing MA (6.50 mL, 0.5 mol L^{-1}), KBrO_3 (7.0 mL, 0.07 mol L^{-1}), H_2SO_4 (6.00 mL, 0.7 mol L^{-1}), and copolymer solution (2.0 mL, 0.4 wt%) was placed in the reactor at $25 \pm 0.1\text{ }^\circ\text{C}$. A CHI-832 electrochemistry analyzer (Shanghai Chenhua Instrument Company, China) was directly connected to the reactor through two Pt electrodes (Rex, 213, China) as the working electrode and the auxiliary electrode and a Hg_2SO_4 reference electrode to record the potential changes.

Measurement of transmittance self-oscillation

The solution was mixed as measurement of potential self-oscillation and stirred until its color began to change between red and light blue at room temperature, then the transmittance

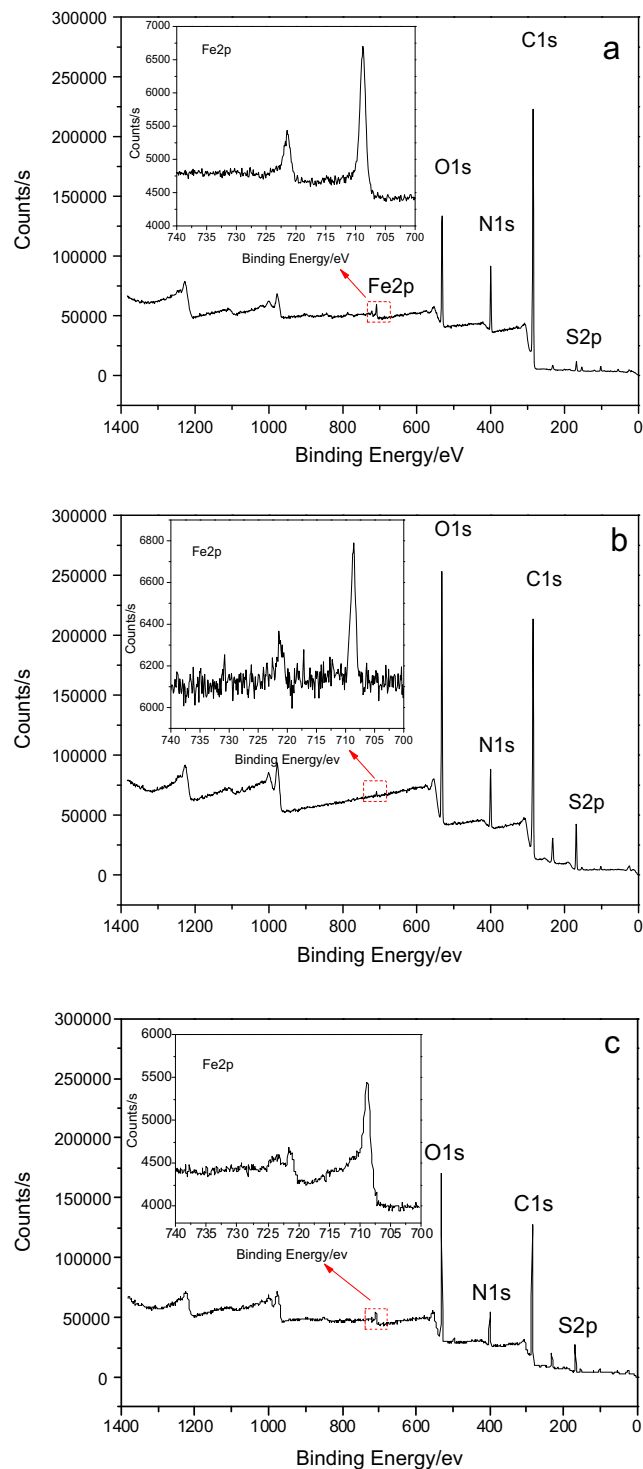


Fig. 4 The XPS spectra of prepared copolymers (**a** P90-10, **b** P50-50, **c** P20-80)

Table 2 The atomic contents of each element in the copolymers

Name	P100-0	P90-10	P50-50	P20-80
C1s	74.91	72.95	61.06	47.28
O1s	13.91	14.14	23.66	18.85
N1s	10.72	10.7	9.16	23.26
Fe2p	0.47	0.68	0.32	0.74
S2p		1.53	5.8	9.16

self-oscillation was measured. A wavelength of 398 nm was also used because of being the isosbestic point of the reduced and oxidized states of the copolymer chain. The time course of the transmittance at 398 nm was monitored using the UV-Vis spectrophotometer (TU-1901, Beijing Purkinje General Instrument Co., Ltd).

Results and discussion

FT-IR spectroscopy analysis

The FT-IR spectra of the copolymer P90-10 (a), copolymer P20-80 (b), and copolymer P50-50 (c) are shown in Fig. 2. It can be seen that the FT-IR spectra are similar. The absorption peaks around 1540 and 1450 cm^{-1} attribute to the C=N stretching vibration and the C=C stretching vibration, respectively. The C-H bending vibration absorption peaks appear at 855 and 730 cm^{-1} . These are the characteristic absorption peaks of phen ring. The absorption peaks at 2975, 2927, and 2866 cm^{-1} attribute to the stretching vibration $-\text{CH}(\text{CH}_3)_2$ group in NIPAAm and the bending vibration of it appears near

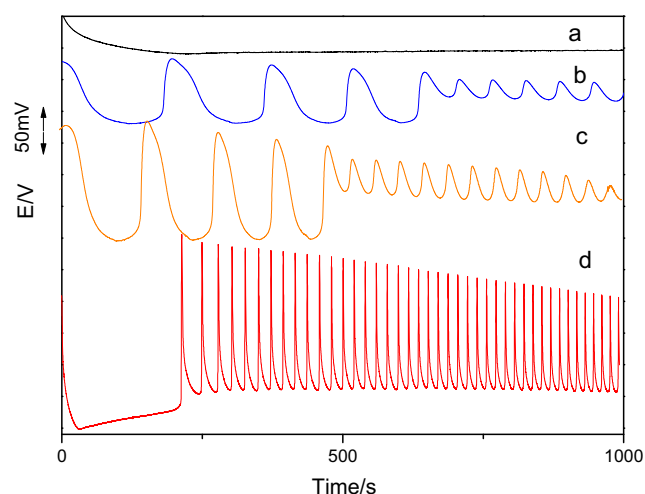


Fig. 5 Typical oscillation waveforms of redox potential of copolymers under the acid-free conditions (a P100-0, b P90-10, c P50-50, d P20-80). The common conditions are as follows: [copolymer]₀ = 0.40 wt%, [KBrO₃]₀ = 0.05 mol/L, [MA]₀ = 0.15 mol/L, and temperature: 25 °C

1375 cm^{-1} . The characteristic absorption peaks of $-\text{SO}_3\text{H}$ are observed at 1230, 628, and 520 cm^{-1} [16]. These observations clearly indicate that the poly(NIPAAm-*co*-AMPS-*co*-Fe(phen)₃) were prepared successfully.

¹H NMR spectroscopy analysis

The ¹H NMR spectra of the copolymer P90-10, copolymer P20-80, and copolymer P50-50 are similar for only different ratios of monomer. Therefore, the ¹H NMR spectrum of copolymer P20-80 was chosen to analyze the chemical structure in the Fig. 3. The singlet at $\delta = 4.61$ was the solvent peak of D₂O. The signals for 1,10-phenanthroline rings were observed between 7.12 and 8.55 ppm [17]. Due to the substituents, the steric hindrance, and the shielding effect, the chemical shift moved to the low field slightly. The singlet at $\delta = 1.18$ attributed to the hydrogens of two methyl in AMPS. The peaks at $\delta = 5.25$ – 6.11 were from three hydrogens on the double bond of carbon atoms. The hydrogen in the group $-\text{SO}_3\text{H}$ exchanged with the deuterohydrogen (D) in the solvent D₂O namely H–D exchange, so the spectral peak could not be displayed. In addition, the hydrogen connected with the nitrogen atom suffered from shielding effect of steric hindrance group $-\text{C}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{H}$ could not exchange with the deuterohydrogen(D), which displayed a singlet at $\delta = 3.42$ [20].

XPS analysis

The XPS method was used to analyze the composition of the obtained copolymers. The results are shown in Fig. 4. XPS analysis revealed the existence of carbon, oxygen, nitrogen, iron, and sulfur in the resulting copolymers. A Fe2p bonding energy of 707.5 eV and a S2p bonding energy of 165 eV were

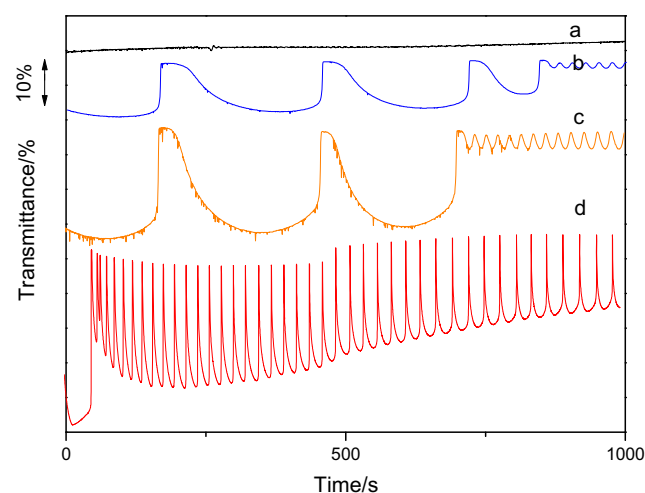


Fig. 6 Typical oscillation waveforms of transmittance self-oscillation of copolymers under the acid-free conditions (a P100-0, b P90-10, c P50-50, d P20-80). The experimental conditions are the same as those in Fig. 5

observed in the three obtained AMPS-containing copolymers. The two-dimensional element images show that iron and sulfur are uniformly dispersed in the copolymers. The atomic composition of each element in the copolymers is listed in Table 2. The atomic composition of sulfur is in the range of 1.53–9.16 %, and it was increased with the increasing AMPS added. These results demonstrated that different AMPS-containing copolymers were obtained.

The effects of AMPS contents on the self-oscillation

The overall process of the BZ reaction is the oxidation of an organic substrate such as citric or malonic acid by an oxidizing agent (bromate) in the presence of metal catalyst under acidic conditions [21]. During the reaction, the metal catalyst can change periodically between reduced state and oxidized state via a single electron transition redox reaction and the organic acid is oxidized into CO_2 , H_2O , and other products [22]. For the BZ oscillating chemical system, the concentration of H_2SO_4 is very important on the parameter. In order to investigate the effect of AMPS contents on the self-oscillating characteristics, H_2SO_4 was substituted with the same volume of deionized water in BZ system and the results are shown in Figs. 5 and 6. It can be seen from the figures that no self-oscillation was observed for P100-0 which was without AMPS in an acid-free BZ system, whereas the other three exhibited varied self-oscillation. It was demonstrated that AMPS was incorporated into the copolymer chain. The $-\text{SO}_3\text{H}$ contained in the AMPS could supply H^+ and let the self-oscillation of the AMPS-containing copolymer chain happen normally under acid-free conditions.

The higher the concentration of H_2SO_4 in BZ system, the higher the frequency of the oscillations is observed [23]. The oscillating period and waveform for the poly(NIPAAm-*co*-Fe(phen)₃-*co*-AMPS) solutions were much affected by the copolymer composition from the figures. Two distinct regimes of oscillation with different amplitudes and periods appeared for P90-10 and P50-50 in BZ system: long period (2–3 min) and short period (50–60 s). However, the amplitudes of both regimes for P50-50 are bigger than those of P90-10 because of the higher AMPS contained. A stable and regular self-oscillating waveform was observed in batch and the oscillation could last several hours as the classical BZ reaction for P20-80 which was with more AMPS. The various patterns for different copolymer compositions originated from the complex mechanism of BZ reaction. However, the amplitudes of redox potential and transmittance self-oscillation decreased gradually and oscillation disappeared finally until the system reached the equilibrium state due to consumption of reactants just like classical BZ reaction. Moreover, the amplitudes of transmittance self-oscillation for the AMPS-containing copolymers are much bigger in comparison with the poly(NIPAAm-*co*-Fe(phen)₃), which we studied previously,

and Ru(bpy)₃-containing smart materials. This is of great advantage in a variety of applications.

In generally, the nonlinear chemical systems are sensitive to external conditions, such as temperature and the concentration of substrates. It is very important to cause self-oscillation in biological environments for such smart materials, and the practical scope as bio-machines can be greatly expanded. By introducing an acid site into the copolymer chain, it was not necessary to add a strong acid to the surrounding solution. Thus, this makes it possible to use self-oscillating copolymers and gels under biological conditions as novel smart materials.

Conclusions

A novel self-oscillating copolymer poly(NIPAAm-*co*-Fe(phen)₃-*co*-AMPS) which underwent soluble–insoluble self-oscillation with big amplitude was obtained. The copolymer has three advantageous characteristics. One is to enable self-oscillation with big amplitude in a BZ system free of strong acid. The other is to self-oscillate for a long time without intermolecular aggregation among the copolymer chains. The third is the oscillating parameters controlled by the content of AMPS in the copolymer. This achievement of self-oscillation of copolymer chains under acid-free conditions may lead to their use as biomimetic materials under physiological conditions.

Acknowledgments The financial support of the Basic Project of Science and Research of Colleges and Universities of Gansu Province (5001-109) and Project for Young Teacher of Northwest Normal University (NWNLU-LKQN-13-6) are acknowledged.

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

Funding The present study was funded by the Basic Project of Science and Research of Colleges and Universities of Gansu Province (5001-109) and Project for Young Teacher of Northwest Normal University (NWNLU-LKQN-13-6).

References

1. Yoshida R, Takahashi T, Yamaguchi T, Ichijo H (1996) *J Am Chem Soc* 118:5134–5135
2. Yoshida R, Sakai T, Ito Y, Yamaguchi T (2002) *J Am Chem Soc* 124:8095–8098
3. Ito Y, Nogawa N, Yoshida R (2003) *Langmuir* 19:9577–9579
4. Shiraki Y, Yoshida R (2012) *Angew. Chem* 124:6216–6220
5. Yashin VV, Balazs AC (2006) *Macromolecules* 39:2024–2026
6. Field RJ, Koros E, Noyes RM (1972) *J Am Chem Soc* 94:8649–8664

7. Hara Y, Yoshida R (2005) *Langmuir* 21:9773–9776
8. Murase Y, Maeda S, Hashimoto S, Yoshida R (2009) *Langmuir* 25:483–489
9. Hara Y, Takamas S, Maeda S, Hashimoto S, Yoshida R (2005) *J Phys Chem B* 109:23316–23319
10. Hara Y, Yoshida R (2008) *J Phys Chem B* 112:8427–8429
11. Yamamoto T, Yoshida R (2013) *React Funct Polym* 73:945–950
12. Ito Y, Hara Y, Uetsuka H, Hasuda H, Onishi H, Arakawa H, Ikai A, Yoshida R (2006) *J Phys Chem B* 110:5170–5173
13. Nakamaru S, Maeda S, Hara Y, Hashimoto S (2009) Control of autonomous swelling-deswelling behavior for a polymer gel. *J Phys Chem B* 113:4609–4613
14. Hara Y, Fujimoto K, Mayama H (2014) *J. Phys. Chem. B* 118:608–612
15. Hara Y, Mayama H, Fujimoto K (2014) *J Phys Chem B* 118:6931–6936
16. Ren J, Yao MQ, Zhang GC, Yang XC, Gu JF, Yang W (2015) *J Polym Res* 22:44. doi:10.1007/s10965-015-0686-6
17. Arimura T, Mukai M (2014) *Chem Commun* 50:5861–5863
18. Ueno T, Bundo K, Akagi Y, Sakai T, Yoshida R (2010) *Soft Matter* 6:6072–6074
19. Ueki T, Takasaki Y, Bundo K, Ueno T, Sakai T, Akagi Y, Yoshida R (2014) *Soft Matter* 10:1349–1355
20. Pi YY, Liang H, Lv GM (1994) *Oilfield Chemistry* 11:9–12
21. Field RJ, Koros E, Noyes RM (1972) *J Am Chem Soc* 94:8649–8664
22. Field RJ, Schneider FW (1989) *J Chem Edu* 66:195–204
23. Smoes ML (1979) *J Chem Phys* 71:4669–4670