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Green Synthesis of Polycarboxylate Superplasticizers via Aqueous Phase Free Radical Polymerization: Kinetics and Optimization for Sustainable Development

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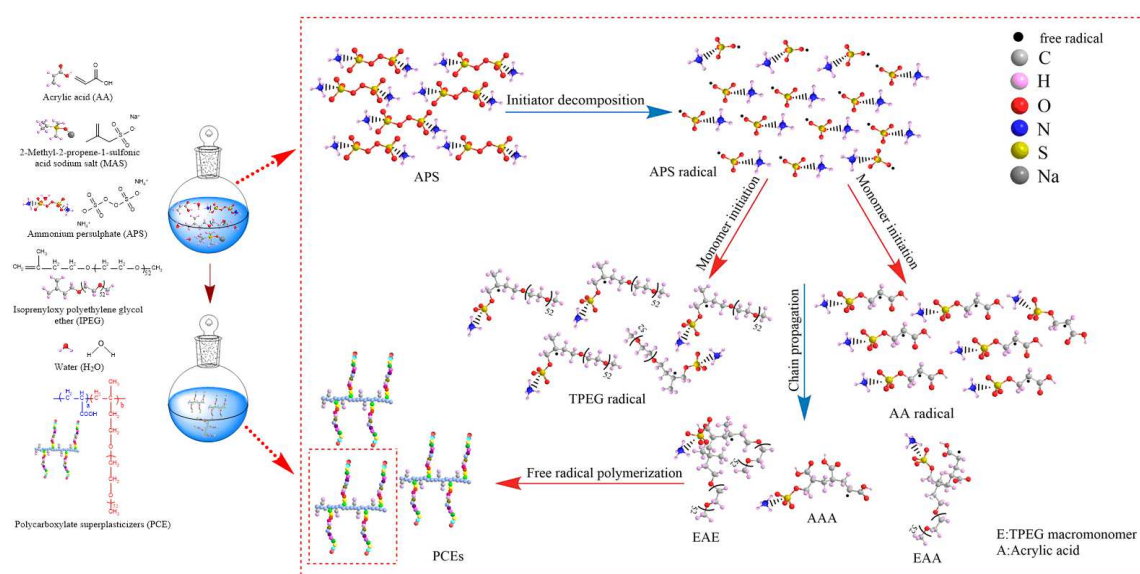
Highlights

1. Aqueous free radical polymerization of PCEs is a pseudo second order reaction.

2. The polymerization rate equation is $R_p \in e^{-1900.4/T} [\text{TPEG}]^{0.68} [\text{AA}]^{0.96} [\text{APS}]^{0.33}$.

3. Polymerization mechanism of PCEs was discussed.
4. Kinetics of PCEs contributes to sustainable concrete development.

Graphic Abstract



Abstract

Polycarboxylate superplasticizers(PCEs) are the most essential chemical admixture of the cement and concrete, which is benefit for dispersing the cement particles, improving the fluidity of mortar and concrete, extending the life of building, reducing the emission of CO₂ and saving energy. To further optimize the synthesis of PCEs and enhance the sustainability of their development, in this study, PCEs were synthesized via radical copolymerization in an aqueous phase free of any organic solvents, and the polymerization mechanism of PCEs was investigated. The molecular weights, polydispersity indexes (PDIs), and functional groups of PCEs were analyzed by size exclusion chromatography (SEC) and Fourier transform infrared (FT-IR) spectroscopy. Next, the concentration of residual monomers, acrylic acid (AA) and isoprenyloxy polyethylene glycol ether (TPEG), in PCEs were determined by SEC and high-performance liquid chromatography (HPLC). Based on the relationship

between concentrations of residual AA and TPEG with the polymerization time, the reaction orders of AA, TPEG, and ammonium persulfate (APS) were fitted and the apparent activation energy of polymerization was calculated. Furthermore, the equation for polymerization rate was derived. Finally, the polymerization mechanism of PCEs was discussed based on the polymerization rate equation. Results showed that in addition to the concentration of monomers and initiator, the polymerization temperature had effects on the molecular weight and PDIs of PCEs, however, not on the functional group. The apparent activation energy of polymerization was $15.8 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$. The aqueous free radical polymerization rate equation of PCEs was: $R_p \in e^{-1900.4/T} [\text{TPEG}]^{0.68} [\text{AA}]^{0.96} [\text{APS}]^{0.33}$. From the equation, the aqueous free radical polymerization of PCEs was found to be pseudo second order reaction. In addition, the polymerization temperature and the concentrations of monomers and initiator affected the aqueous free radical polymerization rate of PCEs. In particular, the concentration of AA was the most significant influencing factor.

Keywords

Sustainability; Free radical polymerization; Polymerization rate equation; Kinetics; Polycarboxylate superplasticizer

1. Introduction

Polycarboxylate Superplasticizers (PCEs), as one of the most widely used chemical admixtures in the cement and concrete industry, not only improve the workability and durability of concrete but also reduce cement consumption and lower CO₂ emissions generated during the clinker calcination process [1-5]. Furthermore, the majority of PCEs on the market are synthesised via radical Polymerization in aqueous solution[6-9] this synthesis process is environmentally friendly and cost-effective, and employs mild reaction conditions making them recognised as green and clean products within the cement and concrete industry [10,11]. Therefore, PCEs are widely used in construction of highways, bridges, tunnels, and for other

engineering projects [12,13]. According to latest study of Global Info Research, the global PCE market was valued at USD 9,560 million in 2025. It is projected to reach USD 13,660 million by 2032, representing a compound annual growth rate (CAGR) of 5.3% between 2026 and 2032.

With the development of the cement and concrete industries, the performance requirements for PCEs are becoming increasingly stringent[14,15]. However, traditional radical polymerization reactions suffer from inherent issues such as uncontrollable reaction processes and broad molecular weight distribution of the products, which may have an adverse impact on the properties of the polymers and their environmental sustainability[16,17]. To better guide the synthesis of PCEs, to precisely control product structure, and to enhance the sustainability of the cement and concrete industries, it is essential to investigate the polymerization kinetics of PCEs. Polymerization kinetics primarily focuses on the quantitative relationships between the polymerization rate and parameters such as initiator concentration, monomer concentration, reaction temperature, and other factors[18]. Amongst reactants, the chain transfer agent only reduces the degree of polymerization, but does not affect its rate[19,20]. The reaction order is an indispensable kinetic parameter that reflects the effect of concentration of reactants (or partial pressure) on the reaction rate, making it an essential part of the reaction mechanism [21,22]. The kinetic equation serves as a guidance for controlling the copolymerization process. It sets the basis for the industrialization of polymerization, which includes the selection of process parameters, influence of various factors on the reaction rate, and the calculations of conversion rate and product yields [23,24]. Palma-Lemus conducted semi-batch aqueous coPolymerization experiments of AA-HPEG in an acidic medium, and investigated the effects of monomer feeding time, initiator concentration and chain transfer agent concentration on the reaction kinetics, HPEG incorporation and molar mass[25]. Tian studied the kinetics of free radical copolymerization of APEG with AA in aqueous medium using ammonium persulfate (APS) and 30% hydrogen peroxide (H_2O_2) as initiators[26]. The relationships between initiator concentration, molar ratio of monomers, polymerization rate, and the apparent activation energy of

polymerization were established. However, the influence of monomers concentration on the polymerization was not discussed separately. Moreover, the kinetics of polymerization, such as polymerization rate equation and polymerization mechanism of PCEs are not well-known.

In this study, to better guide the synthesis of PCEs and enhance sustainability in the green concrete industry, the concentrations of residual monomers in PCEs were determined, the reaction orders of AA, TPEG, and APS were fitted, and the apparent activation energy of polymerization was calculated. Furthermore, the rate equation for polymerization was derived and the polymerization mechanism of PCEs was discussed.

2. Materials and experimental

2.1 Materials

The macromonomers, isoprenyloxy polyethylene glycol ether (TPEG, also referred as IPEG, $M_w = 2400$ g/mol, Industrial grade), were provided by Letian Chemical Co. Ltd., China. 2-Methyl-2-propene-1-sulfonic acid sodium salt (MAS, >98% purity), acrylic acid (AA, >98% purity), ammonium persulfate (APS, >98% purity), and methanol (CH_3OH , $\geq 99.9\%$ purity) were purchased from Aladdin Co. Ltd. Phosphoric acid (HPO_3 , for HPLC, 85-90% purity) and potassium phosphate monobasic (KH_2PO_4 , for HPLC, 99.5% purity) were purchased from Macklin Co. Ltd. Hydroquinone (HQ, >99% purity) were purchased from Xiya Reagent, China. Deionized (DI) water (35.43 $\mu\text{S}/\text{cm}$), prepared in the laboratory, was used for the experiments.

2.2 Experimental methods

2.2.1 Synthesis of PCEs

Four series of PCEs were synthesized from AA and TPEG by free radical copolymerization in aqueous media, following a reported procedure [27]. Series A included PCEs synthesized with different concentration of AA, Series B included PCEs

synthesized with different concentration of TPEG, Series C included PCEs synthesized with different masses of APS, and Series D included PCEs synthesized at different polymerization temperatures. The molar proportions and masses of reactants and the polymerization temperatures are presented in Table1. In a typical procedure, TPEG macromonomer was taken in a 250 mL single-neck round bottom flask equipped with a stirrer and dissolved in DI water. APS dissolved in DI water was designated as initiator solution a. AA monomer and MAS (chain transfer agent) dissolved in DI water was designated as solution b. Then, solutions a and b were fed into the TPEG solution in a single lot. Within 1 h of reaction, 5 mL aliquots of the samples were withdrawn every 5 min, and HQ (0.05 wt% of the total amount of the monomers) was added to terminate the reaction. The reaction scheme and equation are shown in Fig. 1.

Table 1 Molar and mass of reactants, and reaction temperature of PCEs

Samples		$n_{AA}(\text{mol})$	$n_{TPEG}(\text{mol})$	$m_{MAS}(\text{g})$	$m_{APS}(\text{g})$	Polymerization temperature $T(\text{K})$
Series A	PCE-A1	0.0150	0.0100	0.8800	0.2400	343.15
	PCE-A2	0.0250	0.0100	0.8800	0.2400	343.15
	PCE-A3	0.0350	0.0100	0.8800	0.2400	343.15
	PCE-A4	0.0450	0.0100	0.8800	0.2400	343.15
Series B	PCE-B1	0.0250	0.0050	0.8800	0.2400	343.15
	PCE-B2	0.0250	0.0075	0.8800	0.2400	343.15
	PCE-B3	0.0250	0.0100	0.8800	0.2400	343.15
	PCE-B4	0.0250	0.0125	0.8800	0.2400	343.15
Series C	PCE-C1	0.0250	0.0100	0.8800	0.1200	343.15
	PCE-C2	0.0250	0.0100	0.8800	0.2400	343.15
	PCE-C3	0.0250	0.0100	0.8800	0.3600	343.15
	PCE-C4	0.0250	0.0100	0.8800	0.4800	343.15
Series D	PCE-D1	0.0250	0.0100	0.8800	0.2400	333.15
	PCE-D2	0.0250	0.0100	0.8800	0.2400	343.15
	PCE-D3	0.0250	0.0100	0.8800	0.2400	353.15
	PCE-D4	0.0250	0.0100	0.8800	0.2400	363.15

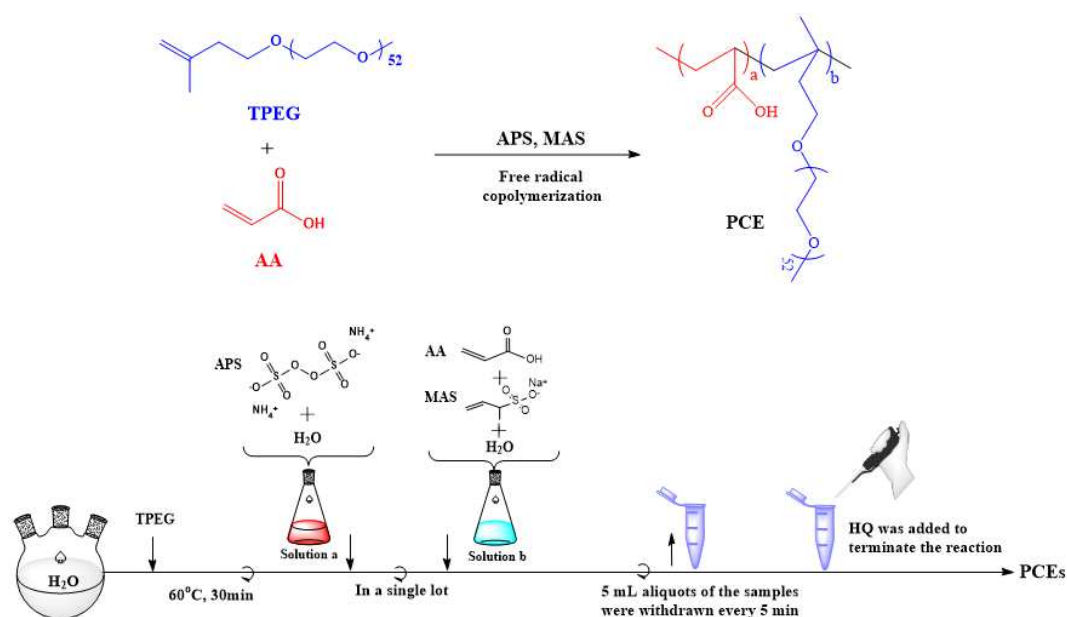


Fig. 1 The reaction scheme and equation for PCEs

2.2.2 Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectra of PCE samples were acquired on a TENSOR 27 FT-IR (Tianjin Port East Technology Development Co. Ltd., China) at 25 °C. The PCE samples were freeze-dried and embedded in KBr pellets in a concentration of about 1 mg/100 mg. The samples were scanned in the spectral range from 4000 to 400 cm⁻¹. The background spectrum was obtained by scanning KBr, prior to the sample analysis.

2.2.3 Molecular weight and polydispersity index of PCEs

The number-average molecular weight (M_n), weight-average molecular weight (M_w), and the polydispersity index (PDI) were determined using Waters1515 (Waters, Eschborn, Germany) SEC system, equipped with two Ultrahydrogel™ columns (120, 500) and a Waters 2414 refractive index detector. A 0.1% aqueous NaN₃ solution was used as an eluent at a constant flow rate of 0.6 mL·min⁻¹. The PCE solutions of 5g·L⁻¹ concentration were used in the SEC measurements, after filtration through 0.22 μm filters.

2.2.4 Quantitative analysis of AA

The quantitative analysis of AA was performed on a L600 high performance liquid chromatograph (HPLC), equipped with a Pgrandsil-STC-C18 column (Beijing Puxi General Instrument Co. Ltd., China). The conditions for the analysis were as follows: the column temperature was 40 °C, the UV detection wavelength was 205 nm, and

injection volumes of eluent were CH_3OH and $0.01 \text{ mol}\cdot\text{L}^{-1} \text{KH}_2\text{PO}_4$ aqueous solution (the pH was adjusted to 2.3 with H_3PO_4) in volume ratio of 5:95, and the individual flow rates were $1 \text{ mL}\cdot\text{min}^{-1}$.

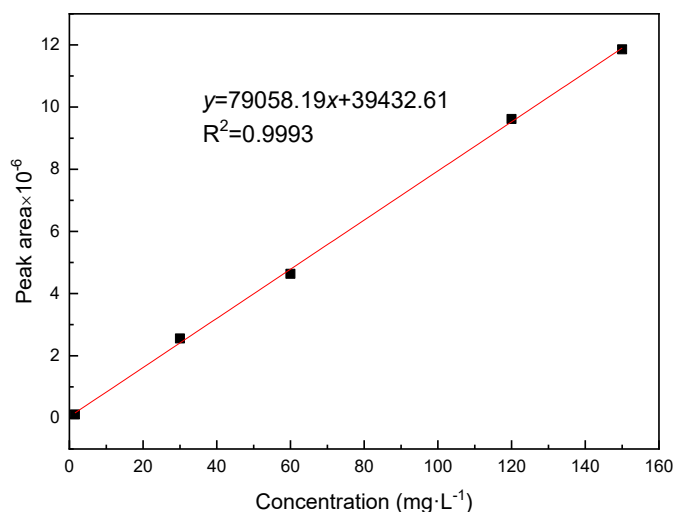


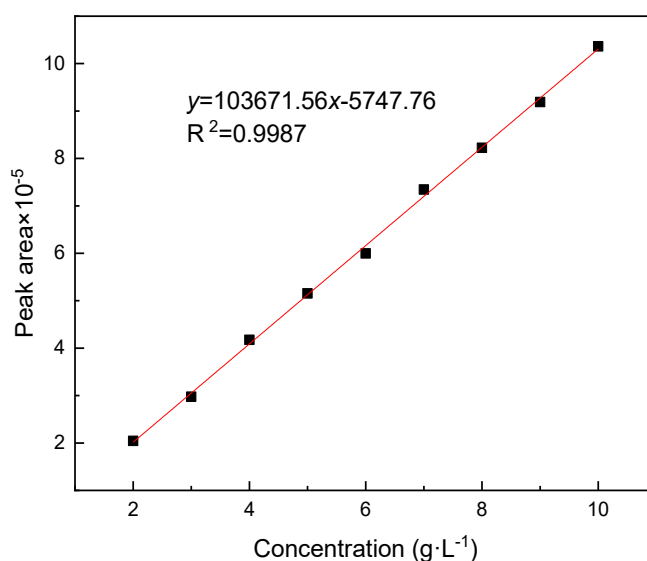
Fig. 2 The standard curve of AA

The standard curve of AA was plotted in the following manner: Firstly, aqueous $0.01 \text{ mol}\cdot\text{L}^{-1} \text{KH}_2\text{PO}_4$ solution (pH adjusted to 2.3 with H_3PO_4) was filtered through a $0.22 \text{ }\mu\text{m}$ membrane and used as a buffer solution. Then, standard AA solutions with mass concentrations of $1.5 \text{ mg}\cdot\text{L}^{-1}$, $30.0 \text{ mg}\cdot\text{L}^{-1}$, $60.0 \text{ mg}\cdot\text{L}^{-1}$, $120.0 \text{ mg}\cdot\text{L}^{-1}$, and $150.0 \text{ mg}\cdot\text{L}^{-1}$ were filtered through a $0.22 \text{ }\mu\text{m}$ membrane and diluted with KH_2PO_4 buffer solution. Next, each AA standard solution was analyzed thrice according to the chromatographic conditions mentioned above and their average values were calculated. Furthermore, the mass concentration of AA standard solution was taken as the abscissa from the standard curve of AA, whereas the corresponding peak area was the ordinate. Finally, the standard curve of AA was fitted. In Fig. 2, the regression coefficient (R^2) of the standard curve of AA was more than 0.99, which indicated that the fitting curve was sufficiently accurate and can be applied for the determining the concentration of AA at any polymerization time for PCEs.

2.2.5 Quantitative analysis of TPEG

The quantitative analysis of TPEG was performed on a Waters1515 (Waters, Eschborn, Germany) SEC system, equipped with two Ultrahydrogel™ columns (120, 500) and a Waters 2414 refractive index detector. An 0.1% aqueous NaN_3 solution was

187 used as the eluent at a constant flow rate of 0.6 mL·min⁻¹.



188
189 Fig. 3 The standard curve of TPEG

190 The following were the steps for plotting the standard curve of TPEG. First, the
191 TPEG standard solutions with mass concentrations of 2.0 g·L⁻¹, 3.0 g·L⁻¹, 4.0 g·L⁻¹, 5.0
192 g·L⁻¹, 6.0 g·L⁻¹, 7.0 g·L⁻¹, 8.0 g·L⁻¹, 9.0 g·L⁻¹, and 10.0 g·L⁻¹ were filtered through 0.22
193 μm aqueous membrane. Next, each TPEG standard solution was analyzed thrice
194 according to the chromatographic conditions mentioned above and the average value
195 was calculated. Further, the mass concentration of TPEG was taken as the abscissa of
196 the standard curve of TPEG, whereas the corresponding peak area was the ordinate.
197 Finally, the standard curve of TPEG was fitted. As shown in Fig.3, the R² of the
198 standard curve of TPEG was above 0.99, which indicated that the curve fitting was
199 sufficiently accurate and can be applied for the determination of concentration of
200 TPEG at any polymerization time in PCEs.

201 2.2.5 Conversion rate and polymerization rate

202 2.2.5.1 Conversion rate

203 The conversion rate was calculated using Eq. (1):

$$204 \quad a = \frac{[M]_0 - [M]_t}{[M]_0} \times 100\% \quad (1)$$

205 Where, a is the conversion rate of M, M represents the monomers (AA and TPEG),
206 $[M]_0$ is the initial concentration of M (mol·L⁻¹), and $[M]_t$ is the concentration of M at
207 any polymerization time t (mol·L⁻¹).

2.2.5.2 Polymerization rate

The initial time period (0-1800 s) of polymerization was significant, and hence the polymerization rate studied in this paper was the average polymerization rate during this initial period.

The polymerization rate R_p was calculated by Eq. (2):

$$R_p = -\frac{[M]_{1800} - [M]_0}{1800} \quad (2)$$

Where, R_p is the polymerization rate ($\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$), and $[M]_{1800}$ is the concentration of M at polymerization time 1800 s ($\text{mol} \cdot \text{L}^{-1}$), the denominator 1800 stands for period of polymerization, which is 1800 s.

2.2.6 Reaction order

The polymerization rate equation of PCEs in aqueous solution is shown as Eq. (3):

$$R_p = k[AA]^\alpha [\text{TPEG}]^\beta [\text{APS}]^\gamma \quad (3)$$

Where, k is the polymerization rate constant ($\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) and α , β , and γ are the reaction orders of AA, TPEG, and APS, respectively.

Log of Eq. (3) can be represented as Eq. (4):

$$\ln R_p = \ln k + \alpha \ln[AA] + \beta \ln[\text{TPEG}] + \gamma \ln[\text{APS}] \quad (4)$$

When the polymerization temperature and the concentrations of TPEG and APS were fixed, Eq. (4) could be simplified to Eq. (5) :

$$\ln R_p = \alpha \ln[AA] + C_1 \quad (5)$$

Where, $C_1 = \ln k + \beta \ln[\text{TPEG}] + \gamma \ln[\text{APS}]$.

The value of α can be derived by plotting $\ln R_p$ as a function of $\ln[AA]$.

In the same way, when the polymerization temperature and concentrations of AA and APS were fixed, Eq. (4) could be simplified to Eq. (6):

$$\ln R_p = \beta \ln[\text{TPEG}] + C_2 \quad (6)$$

Where, $C_2 = \ln k + \alpha \ln[AA] + \gamma \ln[\text{APS}]$.

The value of β can be derived by plotting $\ln R_p$ as a function of $\ln[\text{TPEG}]$.

When the polymerization temperature and the concentrations of AA and TPEG were fixed, Eq. (4) can be simplified to Eq. (7):

$$\ln R_p = \gamma \ln[\text{APS}] + C_3 \quad (7)$$

Where, $C_3 = \ln k + \alpha \ln[\text{AA}] + \beta \ln[\text{TPEG}]$.

The value of γ can be derived by plotting $\ln R_p$ as a function of $\ln[\text{APS}]$.

2.2.7 Activation energy

The activation energy was determined by Arrhenius equation [28], which is represented as Eqs. (8) and (9):

$$k = A e^{-\frac{E_a}{RT}} \quad (8)$$

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (9)$$

Where, E_a is the activation energy of polymerization reaction ($\text{J} \cdot \text{mol}^{-1}$), which refers to the energy required for the molecule to change from a normal state to an active state, A is pre-exponential factor, and R is the ideal gas constant having a value of $8.314 \text{ (J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$, and T is the polymerization temperature (K).

When the concentrations of TPEG, AA, and APS were fixed, Eq. (4) could be combined with Eq. (9) to obtain Eq. (10):

$$\ln R_p = -\frac{E_a}{RT} + \ln A + C_4 \quad (10)$$

Where, $C_4 = \alpha \ln[\text{AA}] + \beta \ln[\text{TPEG}] + \gamma \ln[\text{APS}]$. By plotting a series of $(T^{-1}, \ln R_p)$, the activation energy E_a can be obtained from the slope of the straight line.

3. Results and discussion

3.1 Fourier transform infrared (FT-IR)

The functional groups of PCE polymers were analyzed by FT-IR spectroscopy. The FT-IR spectra of the four series of PCEs are shown in Fig. 4. In Fig. 4, peak for –OH stretching vibrations of carboxyl group ($-\text{COOH}$) was observed at 3400 cm^{-1} . Peaks for C-H stretching vibrations and bending vibration of alkyl ($-\text{CH}_2-$) were observed at 2900 cm^{-1} and 1457 cm^{-1} , respectively. Besides, peaks for C=O stretching vibrations of carboxyl ($-\text{COOH}$) appeared at 1727 cm^{-1} . Peak for the C-H bending vibrations of methyl ($-\text{CH}_3$) was observed at 1350 cm^{-1} . Furthermore, the peak for C-O-C stretching vibrations of polyoxyethylene ($-(\text{CH}_2\text{CH}_2\text{O})_{52}-$) was observed at 1108

cm⁻¹. These results demonstrated the successful syntheses of PCEs [29,30]. It was also evident that the concentrations of AA, TPEG, APS, and polymerization temperature made no difference to the functional group of PCEs..

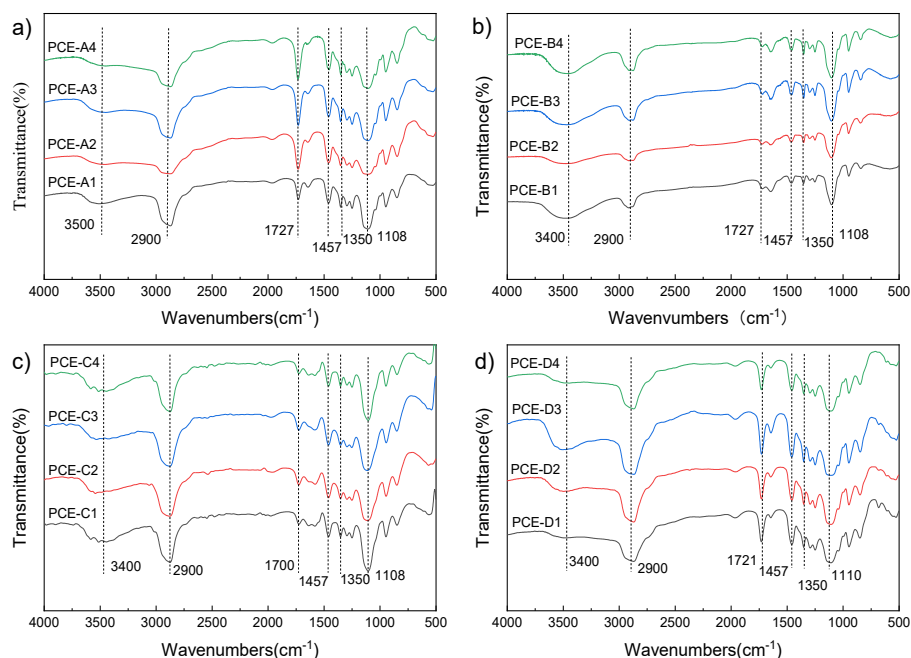


Fig. 4 FT-IR spectra of PCEs

a) Series A; b) Series B; c) Series C; and d) Series D

3.2 Molecular weight and polydispersity index of PCEs

The SEC spectra of the four series of PCEs are shown in Fig. 5 and the results of M_n , M_w , and PDI are shown in Table 2 and Figs. 6 and 7. As shown in Table 2 and Fig. 6, the M_n of the PCEs were in the range of 4,000 to 9,000 g·mol⁻¹. The PDI of PCEs was <1.3, which indicated a fairly narrow molecular weight distribution. It was clear that the molar weights and PDI values of the PCEs were strongly affected by the polymerization temperature and concentrations of monomers and initiator.

The molar weights and PDIs of series A and B are presented in Figs. 6 and 7. The M_n and PDI of PCE increased with increase in AA concentration and decreased with increase in TPEG concentration. A possible explanation is that AA is more reactive than TPEG [31]. With increase in acid-to-ether ratio, the more highly reactive AA monomers participated in the polymerization, causing an increase in molecular weight

and PDI. In case of Series C, the molecular weight and PDI increased with the increase in initiator APS concentration, due to the initiation of a greater number of monomers for polymerization. In case of D series, the PDI increased as the polymerization temperature increased. The reason for increase could be that the increase in polymerization temperature made it difficult for the system to dissipate heat, resulting in wider distribution of molecular weight and the PDI increased.

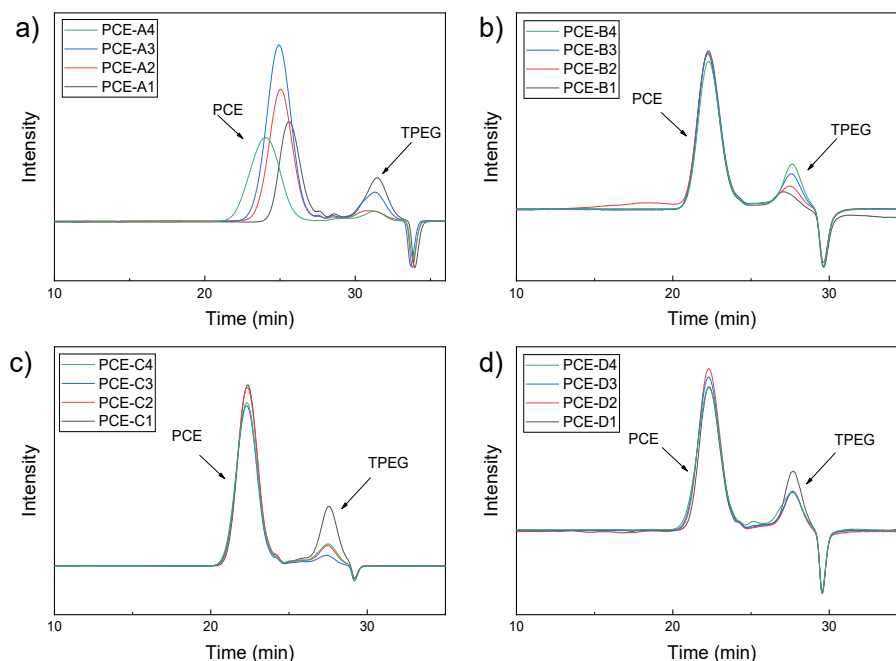


Fig. 5 SEC spectra of PCEs

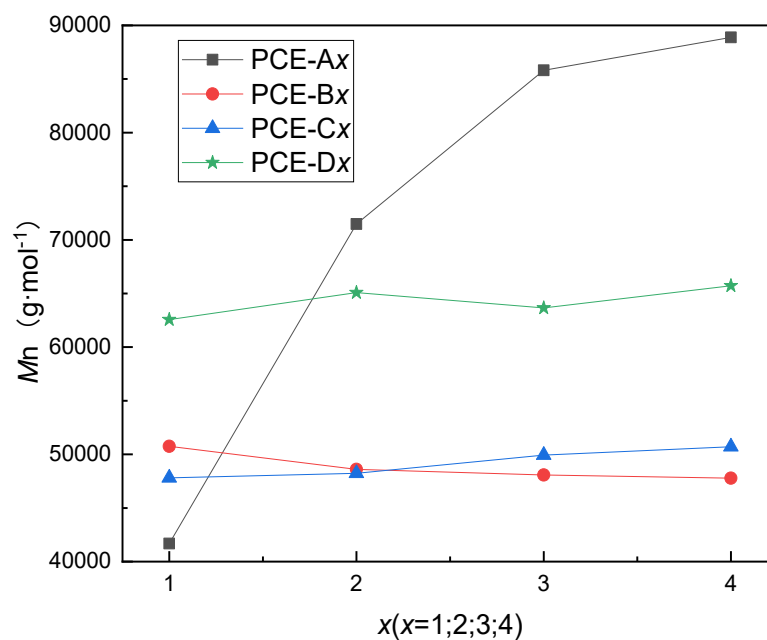
a) Series A; b) Series B; c) Series C; and d) Series D

Table 2 The molar weights and PDIs of PCEs

Samples		M_w (g·mol ⁻¹)	M_n (g·mol ⁻¹)	PDIs
Series A	PCE-A1	55525	41687	1.1908
	PCE-A2	58192	71481	1.2283
	PCE-A3	68975	85806	1.2440
	PCE-A4	70057	88882	1.2687
Series B	PCE-B1	61800	50759	1.2175
	PCE-B2	60074	48600	1.2361
	PCE-B3	59302	48074	1.2336
	PCE-B4	58957	47787	1.2337
Series C	PCE-C1	57110	47806	1.1946
	PCE-C2	58045	48233	1.2103
	PCE-C3	60537	49930	1.2123
	PCE-C4	61961	50712	1.2218
Series D	PCE-D1	72898	62571	1.1617

PCE-D2	76658	65089	1.1675
PCE-D3	75103	63658	1.1786
PCE-D4	78096	65716	1.1818

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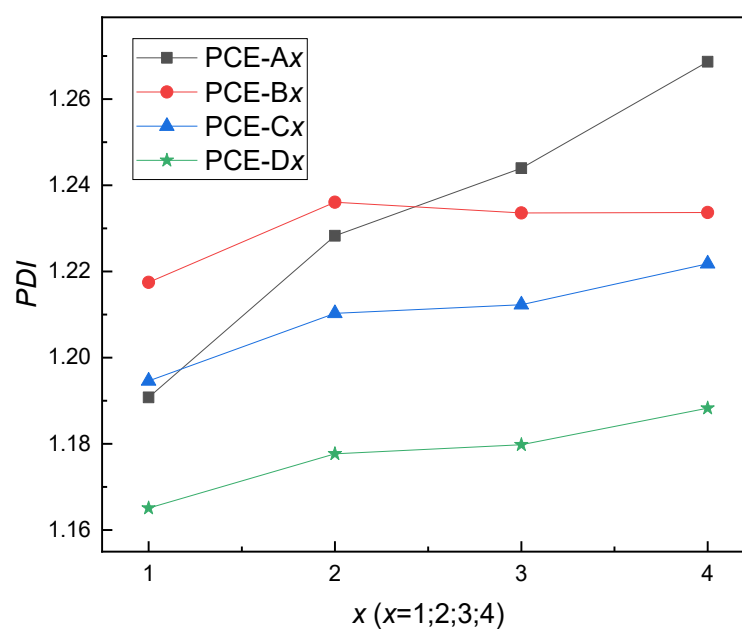


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Fig. 6 M_n values of PCEs

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Fig. 7 PDIs of PCEs

3.3 The polymerization kinetics of PCEs

The basic factors that affect the reaction rate are concentration of the reactants and reaction temperature. Chemical kinetics studies the effects of various factors, such as concentration, temperature, and catalyst on the reaction rate. It also helps to determine the specific steps of the reaction, namely, reaction mechanism. The relation between the reaction rate and concentration of a chemical reaction or the relation between the concentration and time, is called the rate equation of chemical reaction. It is also referred to as the rate equation or the kinetic equation [32].

3.3.1 Reaction order of AA

The conversion rate of AA in the polymerization of Series A is shown in Fig. 8. The polymerization temperature and the concentration of TPEG and APS were fixed. It was evident that the conversion rate increased rapidly at the beginning of the reaction (0~1800 s). However, as the reaction proceeded, it gradually became stable in the later stage (1800~3600 s). Hence, the aqueous free radical polymerization reaction of PCEs was initially fast and then slowed down later. This was due to the one-time feeding employed in the synthesis. Moreover, the concentrations of initiator and monomers were relatively higher in the early stages of reaction, due to which the conversion rate was higher. As the reaction proceeded, the concentrations of the residual monomers decreased gradually, resulting in a slower reaction speed. In series A with different initial concentrations of AA, AA could eventually achieve a high conversion rate, and AA had high reactivity.

The effects of the initial concentration of AA on the polymerization rates of Series A are presented in Table 3. The results revealed that R_p increased with increase in initial concentration of AA. The linear relationship between $\ln R_p$ and $\ln[AA]_0$ is shown in Fig. 9. In Fig. 9, $y = 0.96x - 7.6458$, wherein the slope was 0.96, and hence the reaction order of AA α was 0.96.

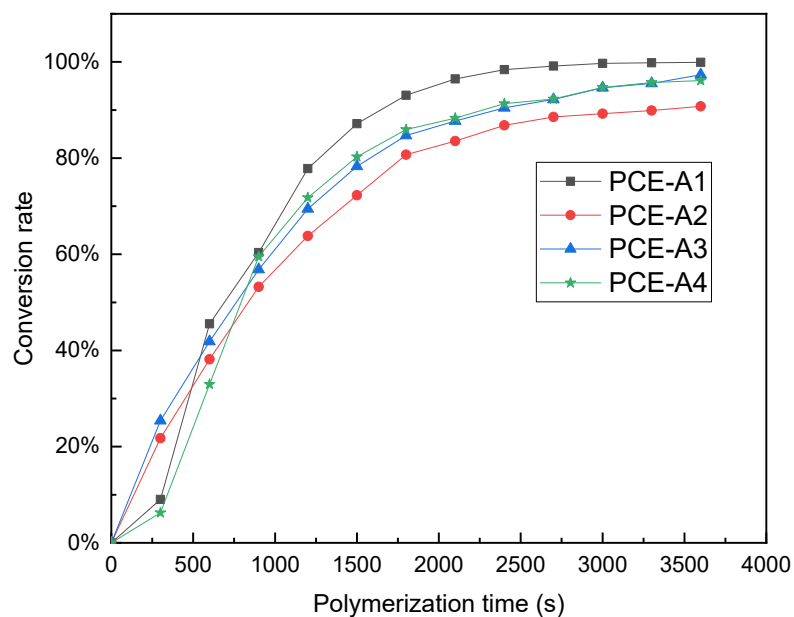


Fig. 8 Conversion rate of AA during the polymerization of Series A

Table 3 Effects of the initial concentration of AA on the polymerization rate of Series A

Series A	Initial concentration of		Polymerization rate	
	AA [AA] ₀ (mol·L ⁻¹)	ln[AA] ₀ (mol·L ⁻¹)	R_p (mol·L ⁻¹ ·s ⁻¹)	ln R_p (mol·L ⁻¹ ·s ⁻¹)
PCE-A1	0.2376	-1.4372	1.3×10^{-4}	-8.9480
PCE-A2	0.4861	-0.7213	2.1×10^{-4}	-8.4684
PCE-A3	0.6643	-0.4090	3.1×10^{-4}	-8.0789
PCE-A4	0.9008	-0.1045	4.8×10^{-4}	-7.6417

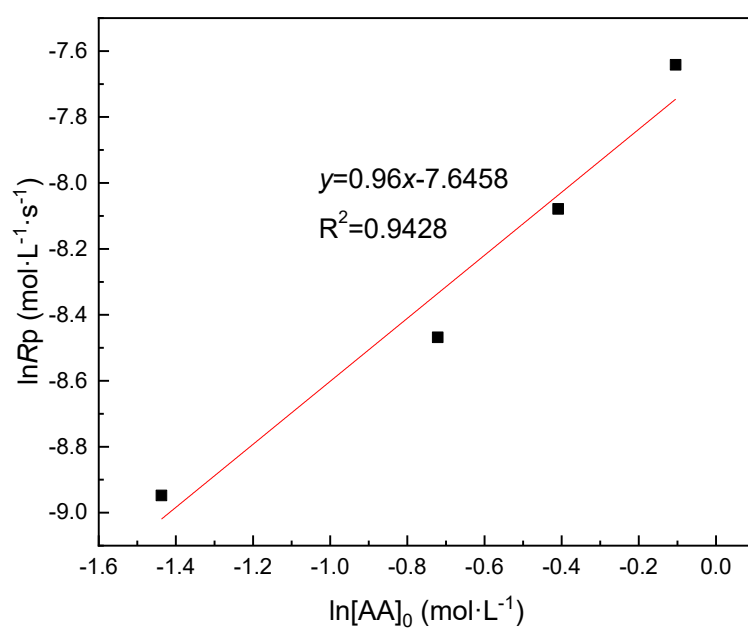


Fig. 9 Relationship between $\ln R_p$ and $\ln[AA]_0$ for Series A

3.3.2 Reaction order of TPEG

The conversion rate of TPEG during the polymerization of Series B is shown in Fig.10, wherein the polymerization temperature and the concentrations of AA and APS were fixed. Fig.10 shows the conversion rate curve of TPEG during the aqueous polymerization of AA with different concentrations of TPEG. Here also the conversion rate was fast initially, but slowed down later on. In case of series B, the higher the initial concentration of TPEG, the lower was the final conversion rate, which indicated that the TPEG reactivity was limited.

The effects of the initial concentration of TPEG on polymerization rate of Series B are presented in Table 4. There was an increase in the value of the R_p with increase in TPEG concentration. The linear relationship between $\ln R_p$ and $\ln[TPEG]_0$ is shown in Fig.10. In Fig.10, $y = 0.68x - 8.5317$, wherein the slope was 0.68 and the reaction order of TPEG β was 0.68.

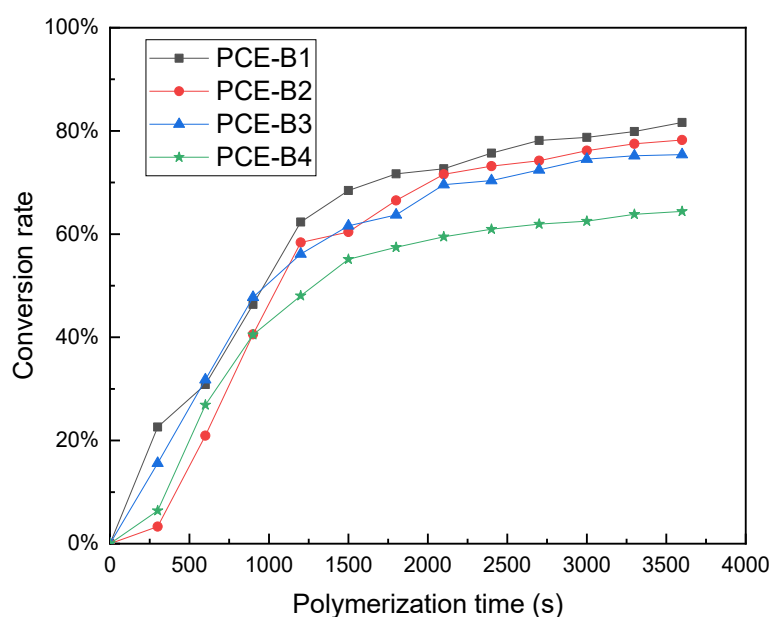


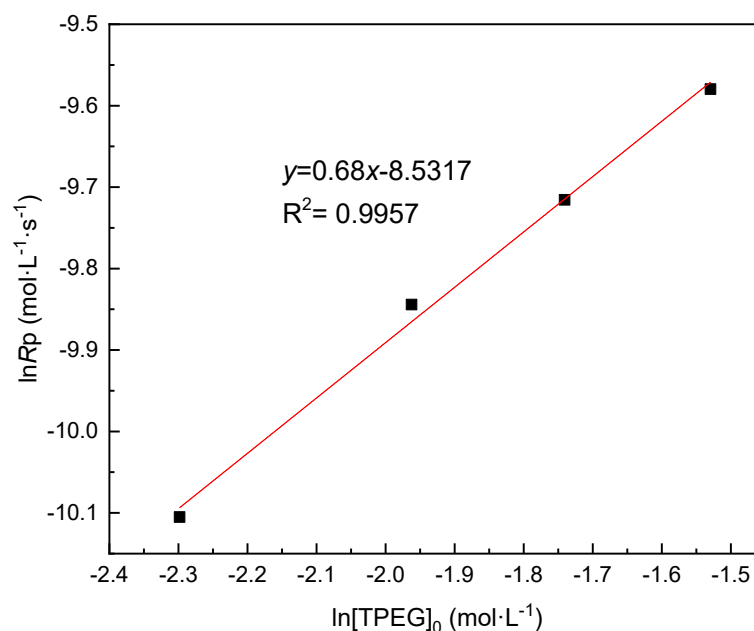
Fig. 10 Conversion rate of TPEG during the polymerization of Series B

Table 4 Effects of the initial concentration of TPEG on polymerization rate of Series B

Series B	Initial concentration of		Polymerization rate	
	TPEG [TPEG] ₀ (mol·L ⁻¹)	ln[TPEG] ₀ (mol·L ⁻¹)	R _p (mol·L ⁻¹ ·s ⁻¹)	lnR _p (mol·L ⁻¹ ·s ⁻¹)

PCE-B1	0.1004	-2.2982	4.1×10^{-5}	-10.1051
PCE-B2	0.1405	-1.9623	5.3×10^{-5}	-9.8443
PCE-B3	0.1754	-1.7406	6.0×10^{-5}	-9.7156
PCE-B4	0.2167	-1.5295	6.9×10^{-5}	-9.5796

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Fig. 11 Relationship between $\ln R_p$ and $\ln[\text{TPEG}]_0$ for Series B

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3.3.3 Reaction order of APS

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The conversion rate of TPEG during the polymerization of Series C is shown in Fig.12, wherein the polymerization temperature and the concentrations of AA and TPEG were fixed. In Fig.12, as the initiator concentration increased, the conversion of the monomer also increased. This result could be explained by the fact that the initiation efficiency increased with increase in initiator concentration. Here, more monomers were induced to form free radicals that participated in the copolymerization reaction. For series C, the more the initial concentration of APS, the higher was the final conversion rate of TPEG. This indicated that the initiator contributed towards the improvement of the final conversion rates of reactants.

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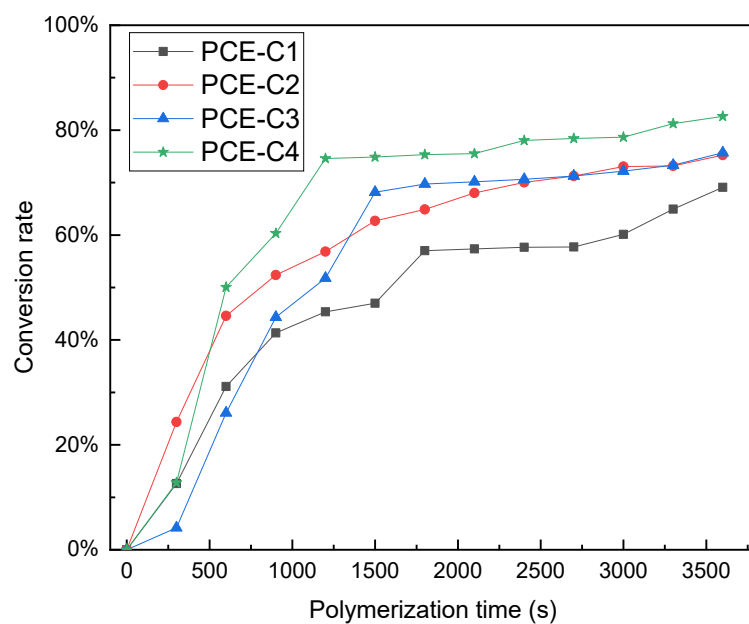
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The effects of initial concentration of APS on the polymerization rates of Series C are presented in Table 5. It was clear that an increase in APS concentration helped to improve the R_p of PCE polymerization. The linear relationship between $\ln R_p$ and $\ln[\text{APS}]_0$ is shown in Fig.13. In Fig.13, $y = 0.33x - 8.3663$, wherein the slope was 0.33,

362 and hence the reaction order of APS γ was 0.33.



363 Fig. 12 Conversion rate of TPEG during the polymerization of Series C

364 Table 5 Effects of the initial concentration of APS on polymerization rates of Series C

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Series C	Initial concentration	$\ln [\text{ASP}]_0$ ($\text{mol} \cdot \text{L}^{-1}$)	Polymerization rate	$\ln R_p$ ($\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$)
	of APS $[\text{APS}]_0$ ($\text{mol} \cdot \text{L}^{-1}$)		R_p ($\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$)	
PCE-C1	0.0087	-4.7536	4.8×10^{-5}	-9.9496
PCE-C2	0.0172	-4.0605	6.5×10^{-5}	-9.6417
PCE-C3	0.0259	-3.6550	6.9×10^{-5}	-9.5808
PCE-C4	0.0345	-3.3673	7.6×10^{-5}	-9.4857

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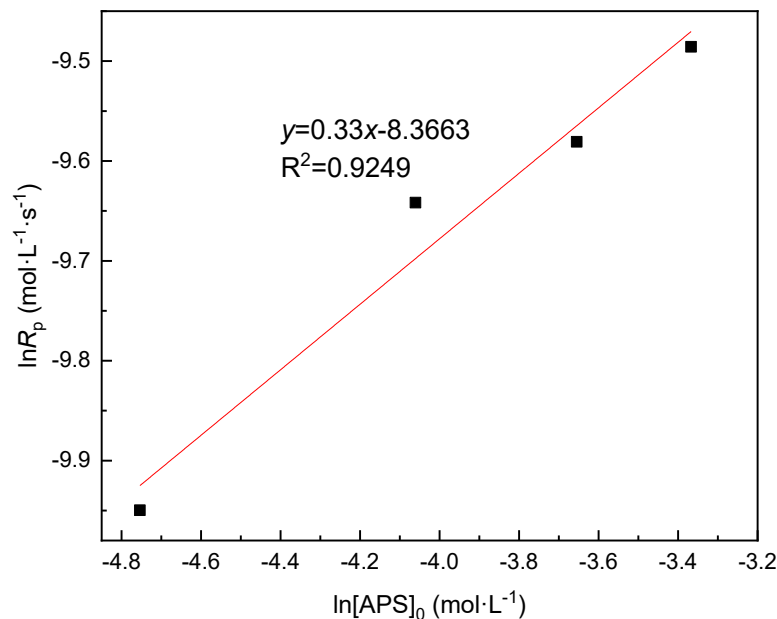


Fig. 13 Relationship between $\ln R_p$ and $\ln[APS]_0$ for Series C

3.3.4 Apparent activation energy

The conversion rate of TPEG during the polymerization of Series D is shown in Fig.14, when the concentrations of AA, TPEG, and APS were fixed. The results significantly indicated an increase in conversion rate with increase in polymerization temperature. This suggested that the system was kinetically controlled[33]. The explanation is that as the polymerization temperature increased, the decomposition of the initiator accelerated. At the same time, at higher temperature, more numbers of free initiator radicals and free monomer radicals were present in the system that could participate in the polymerization. In series D, the higher the polymerization temperature, the higher was the final conversion rate of TPEG. This indicated that the polymerization temperature was also conducive for improving the conversion rate of the reactants.

The effects of polymerization temperature on polymerization rate for Series D are presented in Table 6. In Table 6 that the R_p of PCE increased with increase in polymerization temperature. In Fig. 15, from the plot of $\ln R_p$ against T^{-1} , $y = -1.90x - 4.2631$, the slope of the regression curve was -1.90. According to the Arrhenius equation, the apparent activation energy E_a in the range of 333.15 K-363.15 K was $15.8 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$.

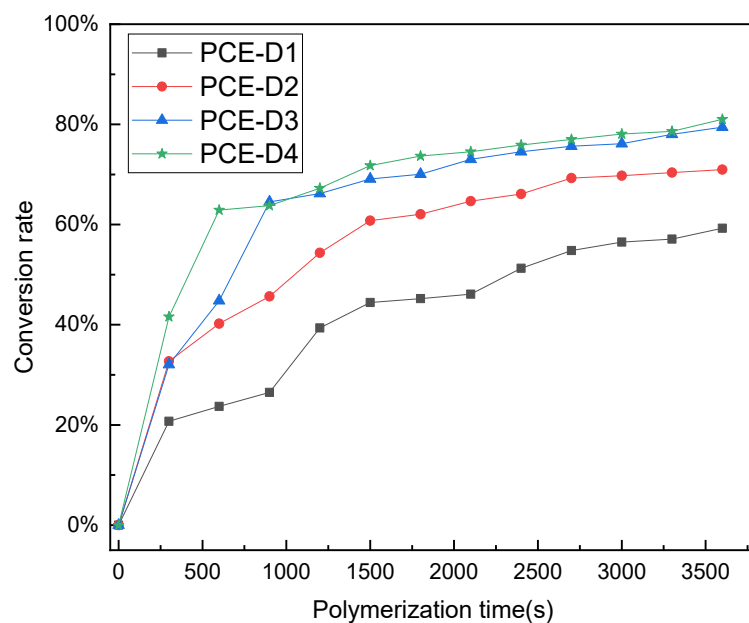


Fig. 14 Conversion rate of TPEG during the polymerization of Series D

Table 6 Effects of polymerization temperature on polymerization rates of Series D

Samples	Polymerization temperature (K)	T^{-1} (K^{-1})	Polymerization rate R_p ($mol \cdot L^{-1} \cdot s^{-1}$)	$\ln R_p$ ($mol \cdot L^{-1} \cdot s^{-1}$)
PCE-D1	333.15	3.0017×10^{-3}	4.5×10^{-5}	-10.0208
PCE-D2	343.15	2.9142×10^{-3}	6.0×10^{-5}	-9.7172
PCE-D3	353.15	2.8317×10^{-3}	6.9×10^{-5}	-9.5759
PC3-D4	363.15	2.7537×10^{-3}	7.1×10^{-5}	-9.5504

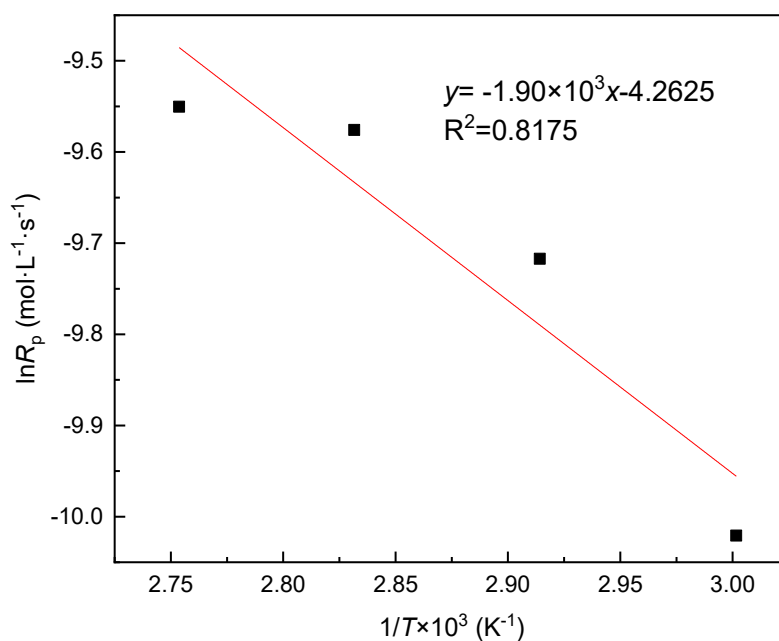


Fig. 15 Relationship between $\ln R_p$ and $1/T$ for Series D

3.4 The mechanism of aqueous free radical polymerization of PCEs

On the basis of the reaction orders of AA, TPEG, and APS and the apparent activation energy described above, the polymerization rate equation was derived as Eq. (11), $R_p \propto e^{-1900.4/T} [\text{TPEG}]^{0.68} [\text{AA}]^{0.96} [\text{APS}]^{0.33}$. It could be concluded that the aqueous free radical polymerization of PCEs was pseudo second order. Polymerization rate and molecular weight are two important indicators for free radical polymerization. Hence, to analyze the factors affecting these two indicators and control methods clearly, the polymerization mechanism should be established.

The aqueous free radical polymerization mechanism of PCEs is schematically shown in Fig.16. In Fig. 16, the polymerization process includes initiator decomposition, chain initiation, and radical polymerization of the monomers. First, the initiator APS undergoes thermal degradation to form primary free radicals. Then, the primary free radicals trigger the formation of AA and TPEG free radicals from AA and TPEG monomers. Finally, the monomer free radicals undergo homopolymerization or copolymerization to PCE polymers.

Based on the polymerization rate equation (Eq. (11)), it was evident that the copolymerization temperature, initiator and monomer concentrations could determine the rate of copolymerization. In the polymerization reaction, AA had the greatest effect on the polymerization rate, which was consistent with other types of polymerization reactions of PCEs [34]. The apparent activation energy E_a for the polymerization system was positive. This indicated that higher the polymerization temperature, the higher is the polymerization rate, which is consistent with the experimental results. Moreover, compared with other types of PCE polymerization processes, the E_a of TPEG-type PCEs was small, indicating that the polymerization of TPEG-type PCEs proceeded in an easier manner [34,26]. Temperature affects the polymerization rate by affecting the decomposition of initiator. The higher the temperature, the faster is the decomposition of the initiator. During free radical polymerization, chain initiation is the slowest step and is the rate controlling step [19].

Chain initiation includes the decomposition of the initiator and chain initiation of the monomer. According to the polymerization rate equation of PCEs, the reaction orders of TPEG and AA were greater than that of APS. Thus, the monomer initiation in chain initiation step has the greatest influence on the polymerization rate.

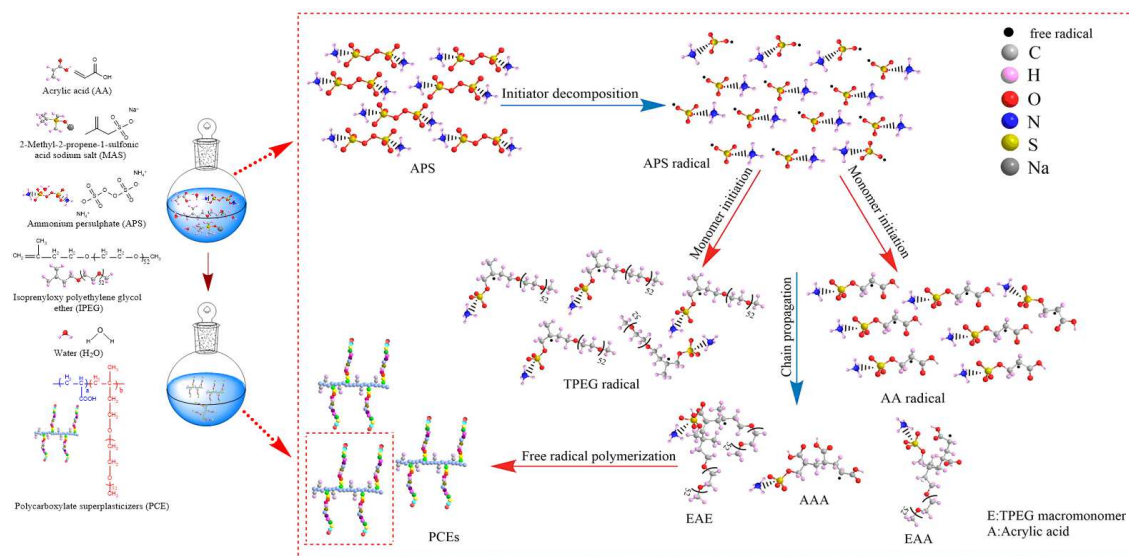


Fig. 16 Reaction mechanism of PCEs

4. Conclusions

The relationship between R_p and initiator, monomer concentrations, polymerization temperature in aqueous free radical polymerization of PCEs was explored in this study. It was found that polymerizations conducted in this study were fast initially and then slowed down. The polymerization temperature and the concentrations of monomers and initiator had a great influence on the molecular weight and PDI of PCEs but made no difference to the functional groups of PCEs. Based on the relationship between R_p and initiator, monomer concentrations, and polymerization temperature, the aqueous free radical polymerization rate equation was derived as:

$$R_p \propto e^{-1900.4/T} [\text{TPEG}]^{0.68} [\text{AA}]^{0.96} [\text{APS}]^{0.33}, \text{ and this reaction was determined to be a}$$

pseudo second order reaction. The apparent activation energy of polymerization reaction in the range of 333.15K-363.15K was $15.8 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$. The polymerization temperature and concentrations of initiator and monomers determined the polymerization rate. AA was found to be the main factor that influenced the

polymerization rate. In the polymerization of PCEs, monomer initiation in the chain initiation step had the greatest influence on polymerization rate.

PCEs are essential polymer additives of the cement and concrete, which is benefit for extending the life of building, reducing the emission of CO₂ and saving energy. Assessment of polymerization mechanism of PCEs on a kinetics level is indeed indispensable for reaction design of effective superplasticizers for concrete technology. All in all, the results reported would provide some research value for industrial production of PCEs and improve their applications in concrete materials, whilst also contributing to the sustainability of the concrete industry.

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