

Study on the relationship between the structure and activities of alkyl methacrylate–maleic anhydride polymers as cold flow improvers in diesel fuels

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Abstract

In order to find efficient cold flow improvers for diesel fuels derived from crude oil, copolymers (R^1MC-MA) were prepared making use of the copolymerization of methacrylate (R^1MC) of various alkyls with maleic anhydride (MA), and terpolymers ($R^1MC-MA-R^2MC$) were prepared by the reaction of long-chain alkyl methacrylate (R^1MC), maleic anhydride (MA), and short alkyl methacrylate (R^2MC). The additives were purified and characterized by IR, ^1H-NMR , and GPC. The activities of the synthetic products as the cold flow improvers in two diesel fuels were investigated. The results indicate that: (1) the alkyl chain length of R^1 in R^1MC-MA copolymers significantly affects the solid point depressing performance. When the long-chain alkyl R^1 is $n-C_{14}H_{29}-$ and the reaction material molar ratio (R^1MC/MA) is 1:2, the $C_{14}MC-2MA$ possesses the best ΔSP property; (2) the ($C_{14}MC-MA-R^2MC$) terpolymers all demonstrate excellent solid point depression properties when the short-chain alkyl R^2 varies from CH_3- to $n-C_8H_{17}-$; (3) however, all of the tested copolymers and terpolymers do not demonstrate necessary cold filter plugging point depression performance.

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Keywords: Alkyl methacrylate–maleic anhydride copolymers; Cold flow improver; Solid point; Cold flow plugging point; Structure–property relations

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1. Introduction

Hydrocarbon fuel oils, for example, petroleum distillate fuels, contain *n*-paraffin waxes that tend to be separated from the oil in low temperature. The waxes generally crystallize as an interlocking network of fine sheets, thereby entrapping the remaining fuel in cage-like structures [1] and causing the cold flow problems such as blockage of fuel lines and filters in engine fuel system. Studies have shown that the network waxes amounting to as little as 1–2 wt.% of the sample are still capable of causing low temperature fluidity and operability problems in distillate fuels [2,3].

In order to alleviate such cold flow difficulties, additives generally referred to as cold flow improvers or pour point depressants have been used. Generally, a cold flow improver contains an oil-soluble long-chain alkyl group and a polar structure moiety in the molecular structure. The long-chain alkyl group can insert into the wax crystal in the fuels, and the polar moiety exists on the surface of the wax crystal, thereby inhibiting the crystal lattice formation and reducing the waxes crystal size [4].

The ethylene–vinyl acetate copolymer is one of the widely used cold flow improvers [5–10] and has good activity in improving the flowing properties of oils. However, the preparation of ethylene–vinyl acetate copolymer needs a high-pressure reaction condition and expensive equipment. Therefore, great efforts have been made to develop other efficient cold flow improvers.

In recent years, increasing attention has been paid to acrylate or methacrylate–maleic anhydride (MA) copolymers used as cold flow improvers [11–15]. However, no report has been available on the influence of the ratios of maleic anhydride to alkyl methacrylate in copolymer as cold flow improvers on their efficiency, and the study on the relationship between the structure of terpolymers with different short-chain alkyl lengths and the cold flow performance has not been reported either.

In this paper, R¹MC–MA copolymers and R¹MC–MA–R²MC terpolymers were prepared and characterized, and the influence of the long-chain alkyl length and the short-chain alkyl length and the reaction material molar ratio on the cold flow performance were investigated.

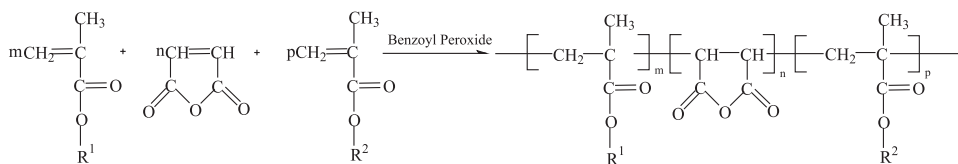
2. Experimental details

2.1. Chemical materials

Four long linear chain alkyl methacrylates (R¹MC, R¹=C₁₂, C₁₄, C₁₆ or C₁₈) were synthesized and purified in our lab with reference to the literature [13]. Four short linear chain alkyl methacrylates (R²MC, R²=C₁, C₂, C₄ or C₈) were bought from the Shanghai Reagent First Factory of China. Technical grade maleic anhydride (MA) was used in the synthesis.

2.2. Preparation of R^1MC –MA copolymers and R^1MC –MA– R^2MC terpolymers

The polymerization reaction is as follows:



A typical process for the polymer synthesis is described as below:

In a 100-ml four-neck round flask fitted with a mechanical stirrer, a condenser, a temperature controller, and a nitrogen-controlled inlet valve, 20 ml of toluene solvent, 14.1 g (0.05 mol) of tetradecyl methacrylate ($C_{14}MC$), and 4.9 g (0.05 mol) maleic anhydride (MA) were added stepwise. Nitrogen gas was flushed through the flask for 30 min, while the reaction mixture was gradually heated. The nitrogen flush was discontinued when the temperature in the flask reached 50 °C. When the temperature of the reaction mixture reached 90 °C, vigorous stirring under nitrogen blanket was applied, and benzoyl peroxide (0.5 wt.%) dispersed in 15 ml of toluene as an initiator was added into the above reaction mixture in equal metered portions every 0.5 h during the first 2 h. The reaction was continued at 90 °C for 6 h.

Copolymers numbered 1–4 of long alkyl methacrylate–maleic anhydride were synthesized using equal molar ratios of both comonomers and following the same aforementioned reaction condition. Copolymers numbered 5 and 6 of tetradecyl methacrylate–maleic anhydride were synthesized under the same conditions except that the comonomers molar ratios were 1:2 and 1:4.

Terpolymers numbered 7–10 of tetradecyl methacrylate–maleic anhydride–short alkyl methacrylate were prepared under the same conditions at a molar ratio of comonomers of 1:2:1.

The copolymers and terpolymers were purified by precipitation in an excess volume of methanol and then separated. Further purification was carried out by dissolution in toluene and reprecipitation with methanol. The process was repeated for several times, and the polymer was vacuum dried at 50 °C for 5 h.

The prepared polymers were analyzed on a NEXUS 670 IR spectroscope, Varian Mercury Plus 400 MHz NMR spectroscope, and DAWN EOS GPC spectroscope, and the results are listed in Table 1.

2.3. The composition of the basic fuels

Two diesel fuels derived from blended crude oils from different oil reserves in Xinjiang of China were used as the basic fuels for evaluating the cold flow performance of the above prepared copolymers and terpolymers as the cold flow improvers. Their physicochemical characteristics are given in Table 2. The data indicate that the carbon number distribution of the total wax in the two fuels is wide and the amount of *n*-paraffins in each of two fuels is higher.

Table 1
The codes and characteristics of the prepared random copolymers and terpolymers

No.	Sample code	Long alkyl R ¹	Short alkyl R ²	Molar ratio R ¹ MC/MA/R ² MC	Mw * 10 ⁴	Polydispersity index
1	C ₁₂ MC–MA	N–C ₁₂ H ₂₅ –		1:1:0	16.87	1.753
2	C ₁₄ MC–MA	N–C ₁₄ H ₂₉ –		1:1:0	16.92	2.204
3	C ₁₆ MC–MA	N–C ₁₆ H ₃₃ –		1:1:0	26.65	1.875
4	C ₁₈ MC–MA	N–C ₁₈ H ₃₇ –		1:1:0	19.84	2.741
5	C ₁₄ MC–2MA	N–C ₁₄ H ₂₉ –		1:2:0	23.59	1.272
6	C ₁₄ MC–4MA	N–C ₁₄ H ₂₉ –		1:4:0	21.03	1.194
7	C ₁₄ MC–2MA–C ₁ MC	N–C ₁₄ H ₂₉ –	CH ₃ –	1:2:1	16.69	1.076
8	C ₁₄ MC–2MA–C ₂ MC	N–C ₁₄ H ₂₉ –	C ₂ H ₅ –	1:2:1	11.11	2.092
9	C ₁₄ MC–2MA–C ₄ MC	N–C ₁₄ H ₂₉ –	n–C ₄ H ₉ –	1:2:1	9.349	2.401
10	C ₁₄ MC–2MA–C ₈ MC	N–C ₁₄ H ₂₉ –	n–C ₈ H ₁₇ –	1:2:1	7.628	2.735

2.4. The evaluating tests of the cold flow performance

The tested diesel fuel samples were prepared individually by respectively mixing the above prepared copolymers and terpolymers (R¹MC–MA and R¹MC–MA–R²MC) with the basic fuel 1 and fuel 2 at a concentration of 500 ppm at 50 °C and stirred for 40 min to guarantee the complete dissolution of the cold flow additives.

The cold flow performance, solid point depression (Δ SP), and cold filter plugging point depression (Δ CFPP) of the tested diesel fuel samples were determined according to SH/T0248 and GB/T 510 standard methods. The solid point depression was determined on a BLY solid point instrument. The method SH/T0248 is similar to the method IP 309.

3. Results and discussion

3.1. Characterization of the chemical structures of copolymers and terpolymers

The chemical structures of the prepared polymers were studied by means of infrared spectrometry. The typical IR spectra of the tetradecyl methacrylate monomer (C₁₄MC),

Table 2
Physicochemical characteristics of the basic diesel fuels

Test	Method	Fuel 1	Fuel 2
Specific gravity 20 °C (kg/m ³)	SH/T 0604	808.1	816.0
Kinematic viscosity at 40 °C (mm ² /s)	GB/T 265	2.062	2.182
Flash point (°C)	GB/T 261	49	49
Cold filter plugging point (CFPP) (°C)	SH/T 0248	–2	–5
Solid point (SP) (°C)	GB/T 510	–9	–10
Total S (μ g/ml)	SH/T 0253	529	399
Saturated hydrocarbon (wt.%)	MS	83.9	79.2
Aromatic hydrocarbon (wt.%)	MS	16.1	20.8
n-paraffins	GC	41.2	36.23
Average carbon number	GC	14.5	14.6
Boiling distillation (°C)	GB/T 6536	152–344	154–348

the copolymer ($C_{14}MC-MA$), and the terpolymer ($C_{14}MC-2MA-C_1MC$) are shown in Fig. 1. By comparing Fig. 1(b,c) with Fig. 1(a), it can be clearly seen that the characteristic CH_3 and CH_2 absorption peaks of long- or short-chain alkyl at 2923 and 2853 cm^{-1} , the characteristic $C=O$ stretching peaks of maleic anhydride at 1853 and 1782 cm^{-1} , and the characteristic $C=O$ strong absorption peak of tetradecyl methacrylate at 1727 cm^{-1} appear in Fig. 1(b,c), and the characteristic $C=C$ stretching vibration peak at 1639 cm^{-1} almost vanishes completely. This indicates that there exist alkyl chain moiety, methacrylate moiety, and maleic anhydride moiety in the prepared copolymers or terpolymers.

The chemical structures of the prepared $C_{14}MC-MA$ copolymers with different ratios were further characterized by ^1H-NMR analysis. The ^1H-NMR spectra of some copolymers are presented in Fig. 2. As seen in Fig. 2, the H of the C–H in polymeric state maleic anhydride shows a chemical shift of 2.83 ppm; the H of the methylene group adjacent to the oxygen atom of tetradecyl shows a chemical shift of 3.93 ppm; the H of the methylene adjacent to the methylene connected with oxygen atom of tetradecyl shows a the chemical shift of 1.61 ppm, the H in the long-chain methylene bands exhibits a chemical shift of 1.26 ppm, and the chemical shifts for the methyl groups are ranged within 0.93–0.86 ppm. This also indicates that there exist alkyl chain moiety, methacrylate moiety, and maleic anhydride moiety in the prepared copolymers.

The prepared copolymers and terpolymers were characterized by determining the average molecular weight, number average molecular weight, and molecular distribution, using a gel permeation chromatographic analysis, and the results are listed in Table 1. The results indicate that the prepared copolymers and terpolymers have average molecular weight from 7.6×10^4 to 26.6×10^4 .

3.2. Influence of the alkyl chain length of the R^1MC-MA on the cold flow performance

The cold flow performance of four R^1MC-MA copolymers with different alkyl chain lengths was evaluated. The results are listed in Table 3. It is seen that the $C_{14}MC-MA$ copolymer with $n-C_{14}H_{29}$ - alkyl chain possesses the best solid point depression performance (ΔSP), whereas the copolymer with $n-C_{12}H_{25}$ - or $n-C_{18}H_{37}$ - almost has no solid point depression performance (ΔSP). According to the general knowledge of the solid point depression [14], the copolymer can co-crystallize with the wax in the diesel fuel to possess good cold flow performance if the side chain length of the copolymer is fit to composition of the wax in the diesel fuel. It is thus concluded that the $n-C_{14}H_{29}$ - alkyl chain is the optimal matching alkyl chain for preparing the cold flow improvers suitable to the tested basic fuels derived from Xinjiang crude oils.

3.3. Influence of the ratio of MA moiety in R^1MC-MA copolymer on the cold flow performance

The R^1MC-MA copolymers can be prepared by controlling the molar ratio of the reaction materials at the same conditions mentioned earlier. But the real molar ratio of the MA moiety in the obtained copolymer may differ from that of the reaction

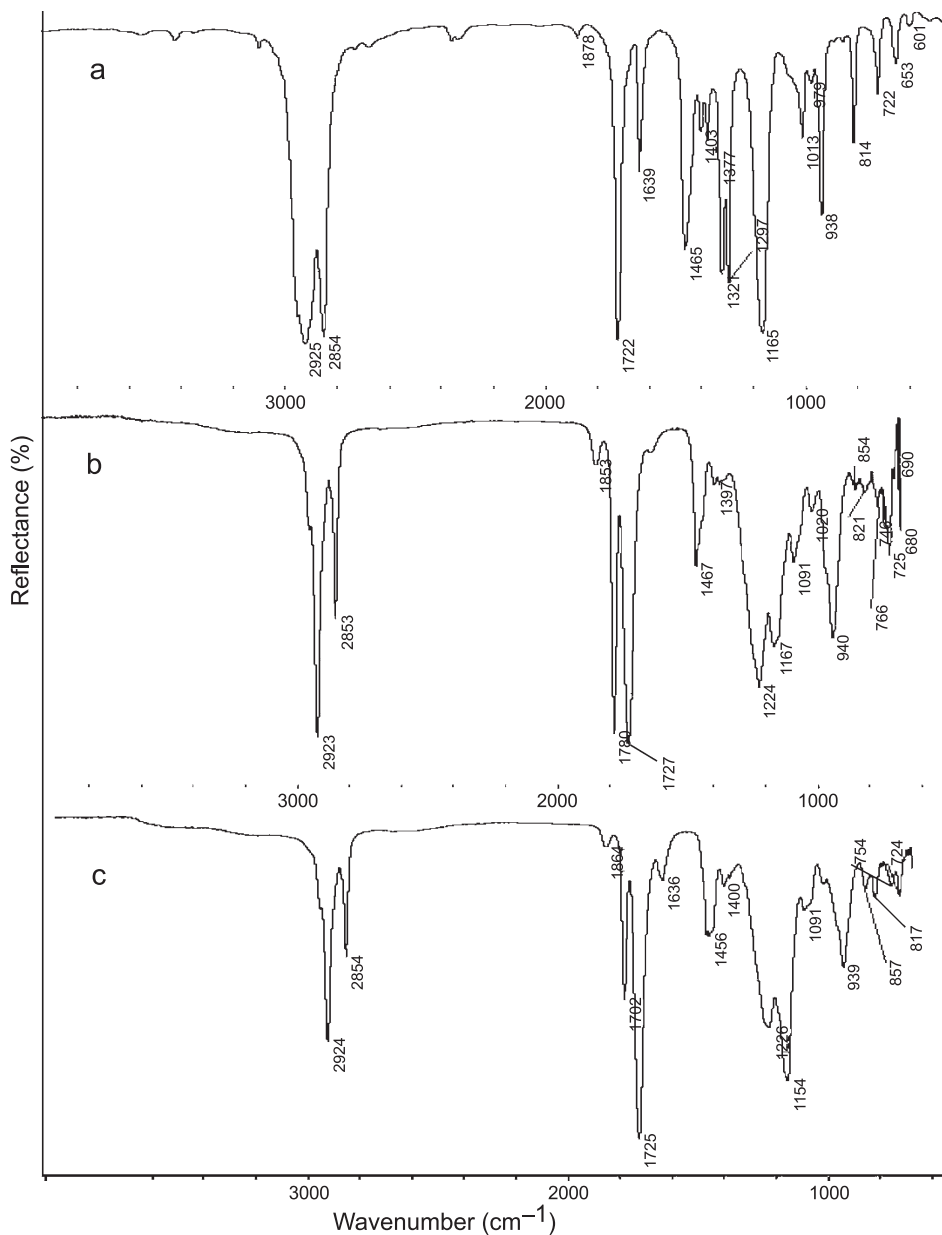


Fig. 1. The IR spectra of $C_{14}MC$ (a), $C_{14}MC-MA$ (b), and $C_{14}MC-2MA-C_1MC$ (c).

materials. It is very important to determine the real molar ratio of the MA moiety in the R^1MC-MA copolymer because the real molar ratio of the MA moiety in the copolymer can directly affect the copolymer structure and further affect its cold flow performance. In this study, ^1H-NMR analysis was carried out to determine the real

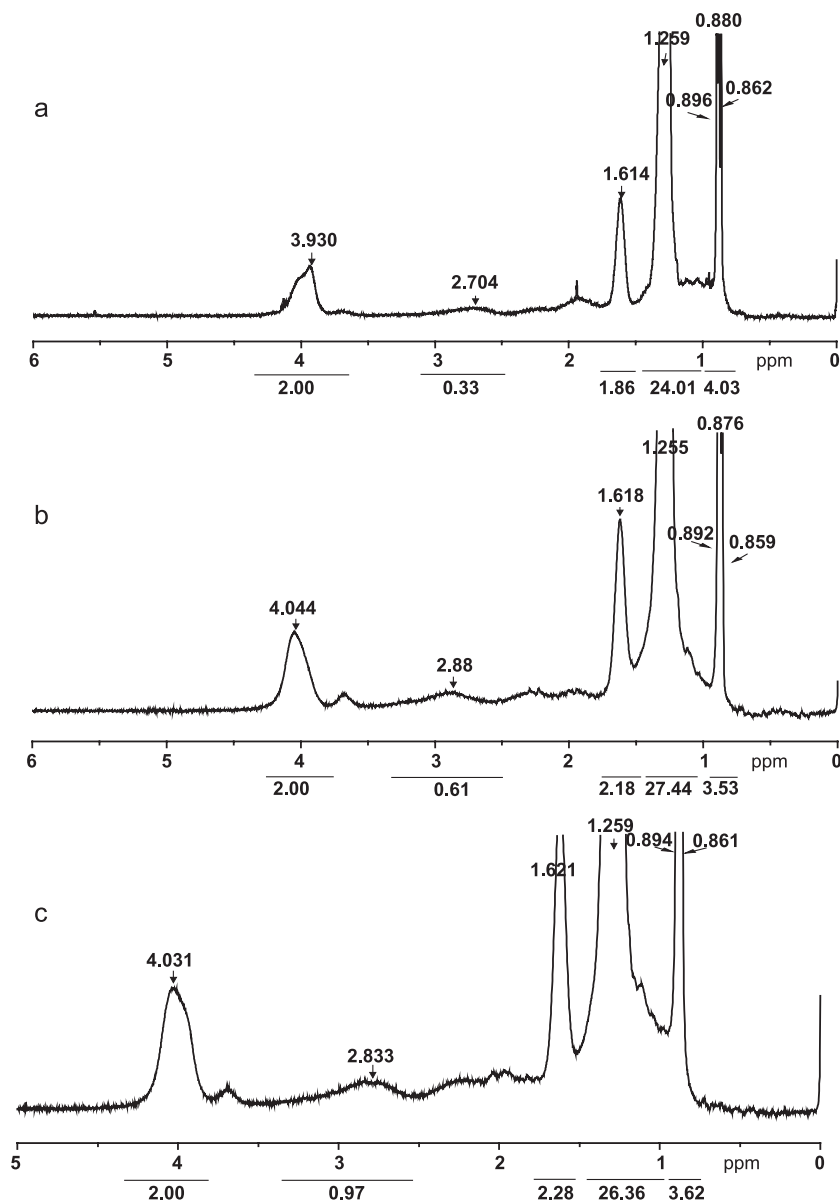


Fig. 2. $^1\text{H-NMR}$ spectra of $\text{C}_{14}\text{MC-MA}$ (a), $\text{C}_{14}\text{MC-2MA}$ (b), and $\text{C}_{14}\text{MC-4MA}$ (c).

molar ratio of the MA moiety in the $\text{C}_{14}\text{MC-MA}$ copolymer with reference to the literature [16]. The real molar ratio of MA moiety in the $\text{C}_{14}\text{MC-MA}$ copolymer was calculated using the following equation:

$$\% \text{MA} = \left[\frac{S_2}{(S_2 + S_1)} \right] \times 100$$

Table 3

The cold flow performance of the R¹MC–MA copolymers with different alkyl chain lengths in diesel fuels (additive concentration: 500 ppm)

R ¹ MC–MA Copolymers			Δ SP (°C)		Δ CFPP (°C)	
Code	R ¹	R ¹ MC/MA	Fuel 1	Fuel 2	Fuel 1	Fuel 2
C ₁₂ MC–MA	<i>n</i> -C ₁₂ H ₂₅ –	1:1	–1	0	0	–1
C ₁₄ MC–MA	<i>n</i> -C ₁₄ H ₂₉ –	1:1	12	13	2	2
C ₁₆ MC–MA	<i>n</i> -C ₁₆ H ₃₃ –	1:1	7	8	1	–1
C ₁₈ MC–MA	<i>n</i> -C ₁₈ H ₃₇ –	1:1	1	4	2	0

Where S₁ and S₂ are the peak areas of the resonance at 3.93 ppm (–O–CH₂– group in tetradecyl methacrylate) and 2.83 ppm (–CH–CH– group in maleic anhydride).

The reaction material ratio, real molar ratio of MA moiety in the C₁₄MC–MA, and the corresponding cold flow performance of the synthetic product are given in Table 4. It is seen that the real ratio of the MA in the copolymer increases with increasing ratio of MA in the reaction materials. At the same time, the cold flow performance of the fuel is improved with increasing real molar ratio of MA in the copolymer, but the performance of the copolymer gradually is worsened when the ratio of maleic anhydride increases to a certain value. This is because a good cold flow improver only needs weak polarity rather than nonpolarity or high polarity [17]. When the polar groups are excess in the molecules, they hinder the co-crystallization of the polymer with the *n*-paraffins in the diesel fuel. Thus, it is suggested to set the ratio of the reaction materials (C₁₄MC/MA) to be 1:2.

3.4. Influence of the short alkyl chain length of C₁₄MC–MA–R²MC terpolymer on the cold flow performance

In order to obtain efficient cold flow improvers, four C₁₄MC–MA–R²MC terpolymers with different short-chain alkyls were prepared and their cold flow performances were evaluated. The results are listed in Table 5. It can be seen that the solid point depression performances of the four terpolymers are excellent as the short-chain alkyl length R² increases from C₁ to C₈. It is thus inferred that the polymer containing short-chain alkyl can promote the polymer to co-crystallize with the *n*-

Table 4

The cold flow performance of R¹MC–MA copolymers with different R¹MC/MA ratios in the diesel fuels (additive concentration: 500 ppm)

R ¹ MC–MA copolymers			Δ SP (°C)		Δ CFPP (°C)	
Code	R ¹ MC/MA	MA (molar %)	Fuel 1	Fuel 2	Fuel 1	Fuel 2
C ₁₄ MC–MA	1:1	14.2	12	13	2	2
C ₁₄ MC–2MA	1:2	23.4	18	17	1	2
C ₁₄ MC–4MA	1:4	32.6	15	19	1	2

Table 5

The cold flow performance of C₁₄MC–MA–R²MC terpolymers with different short alkyl chain lengths in the diesel fuels (additive concentration: 500 ppm)

C ₁₄ MC–MA–R ² MC terpolymer			Δ SP (°C)		Δ CFPP (°C)	
Code	R ²	C ₁₄ MC/MA/R ² MC	Fuel 1	Fuel 2	Fuel 1	Fuel 2
C ₁₄ MC–2MA–C ₁ MC	CH ₃ –	1:2:1	19	19	0	2
C ₁₄ MC–2MA–C ₂ MC	C ₂ H ₅ –	1:2:1	18	18	1	3
C ₁₄ MC–2MA–C ₄ MC	<i>n</i> -C ₄ H ₉ –	1:2:1	18	19	0	2
C ₁₄ MC–2MA–C ₈ MC	<i>n</i> -C ₈ H ₁₇ –	1:2:1	18	21	0	1

paraffins in the fuel. However, the short alkyl chain length is not beneficial to the Δ CFPP performance of the fuel.

4. Conclusions

1. A series of copolymer and terpolymers derivated from alkyl methacrylate and maleic anhydride were prepared, purified, and characterized.
2. Of those tested copolymer products, the R¹MC–MA copolymer with the long-chain alkyl R¹ to be *n*-C₁₄H₂₉– and the reaction material molar ratio (R¹MC/MA) to be 1:2 possesses the best solid point depressing performance. It is imperative to maintain a proper content of polar groups in the polymer molecules so as to improve the solid point depression performance of the fuel; otherwise, an excess amount of the polar groups hinder the polymer co-crystallization with the *n*-paraffins in the diesel fuel.
3. The introduction of short-chain alkyls promotes the polymer to co-crystallize with the chain of *n*-paraffins. The prepared C₁₄MC–MA–R²MC terpolymers possess excellent solid point depression performance when the short-chain alkyl R² varies from C₁ to C₈.
4. All of the tested copolymers and terpolymers cannot obviously improve the cold filter plugging point depressing performance of the diesel fuel.

Acknowledgements

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