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Synthesis of comb bipolymers and their pour point depressing properties

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Abstract: A bipolymer maleic anhydride-methyl acrylate (MAMA) was synthesized from maleic anhydride and methyl acrylate based on molecular design. MAMA further reacted with oleylamine or octadecyl alcohol to generate two comb polymers called Oleamide-MAMA (NMAMA) and Octadecanol-MAMA (OMAMA), respectively. The structure of both the polymers was confirmed by their infrared spectral analysis (IR), gel permeation chromatography analysis (GPC) and differential scanning calorimeter (DSC). Moreover, the pour point depressing (PPD) properties of these comb polymers were examined experimentally. Experimental results showed that besides the molecular weight and concentration of the polymers, the length of side chains and the number of functional groups also had great influence on the pour point depressing performance. The π bonds and hydrogen bonds between depressants were the key factors for improving the pour point depressing properties. These results suggest that both OMAMA and NMAMA are potential pour point depressants for industry.

Key words: Maleic anhydride, comb polymers, pour point depressant, hydrogen bonds, molecular simulation

1 Introduction

With the rapid development of industry worldwide, the demand for crude oil and the production of crude oil is increasing year by year. But most of the oilfields are in the mid-late recovery stage, and the proportion of paraffin wax in crude oil is increasing rapidly, resulting in the crude oil having high viscosity and bad flow performance. The increased viscosity makes crude oil production and pipeline transportation more difficult. Therefore, development of technology for high viscosity crude oil transportation has become an important issue (Yang, 2006; Tokuma et al, 2003).

Currently, crude oil pour point depression is used to solve these problems (Wang et al, 2007; Prahl, 2000). For low-viscosity crude oil, most pour point depressants are synthesized based on ethylene vinyl acetate (EVA) polymer. For high-viscosity crude oil, although the study of pour point depressants based on acrylic ester and maleic anhydride copolymers have been reported (Du et al, 2012), but studies on the effect of functional groups, polymer structure and thermal stability on the paraffin crystallization process are still relatively limited (Deshmukh and Bharambe, 2009; Mieulet, 1966).

In this paper, one bipolymer called MAMA was first synthesized from maleic anhydride and methyl acrylate. Then MAMA reacted with oleylamine or octadecyl alcohol to produce two comb polymers NMAMA and OMAMA, respectively. The structures and properties of the three polymers were studied by infrared spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) (Lehn, 1995; Soni and Kiranbala, 2010; Tang et al, 2009; Zhu, 2012). The paraffin crystallization behavior and pour point depressing properties of the crude oil were also studied from the aspects of polymer functional groups, polymer structures and thermal stability.

2 Experimental

Free radical polymerizations are mainly bulk polymerization, solution polymerization, emulsion polymerization and suspension polymerization (Pan, 2007). Considering the difficulty in operation of their technological processes, the solution polymerization and emulsion polymerization are usually adopted (Beristain et al, 2012; Allan et al, 2012); They are also suitable for the copolymerization of acrylic ester and maleic anhydride. But in emulsion polymerization method, it is not easy to

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control the molecular weight of the polymers, and polymers with large molecular weight usually have bad oil solubility. Therefore, we adopted the solution polymerization method (Galicia et al, 2011; Frauendorfer and Hergeth, 2011) in this work.

2.1 Raw materials

The materials used in experiment are shown in Table 1.

Table 1 Raw materials

Materials	Purity	Manufacturer
Maleic anhydride	AP	Tianjin Kemiou Chemical Reagent Co., Ltd., China
Acrylic acid methyl ester	AP	Shanghai Chemical Reagent company, China
ABIN	AP	Shanghai Hervey Chemical Industrial limited company, China
High pure nitrogen	99.99%	Ji'nan Deyang Special Gas Company, China
Oleylamine	AP	J&K Scientific Ltd., China
Octadecyl alcohol	AP	Tianjin Damao Chemical Reagent factory, China
Benzene	AP	Laiyang Kangde Chemicals Co., Ltd., China
Tetrahydrofuran	AP	Sinopharm Chemical Reagent Co., Ltd., China
Hexane	AP	Tianjin Damao Chemical Reagent factory, China
Ethanol	AP	Tianjin Fuyu Fine Chemical Co., Ltd., China

2.2 Experimental device

The experimental device is shown in Fig. 1

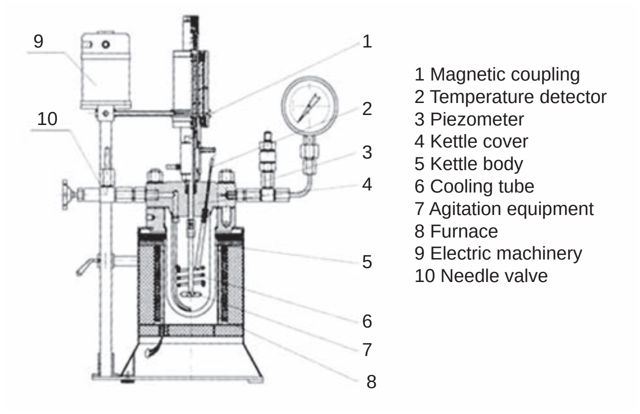
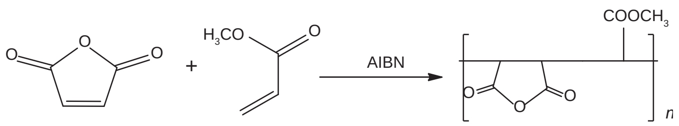


Fig. 1 Experimental device for emulsion polymerization—GSH reactor

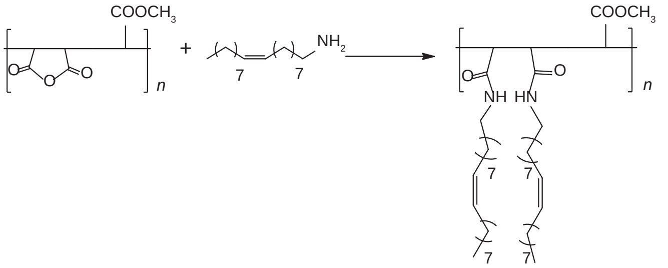
2.3 Preparation of MAMA

The mixture of acrylic acid methyl ester and maleic anhydride (in a molar ratio of 1:1) was dissolved in benzene in a polymerization reactor which was equipped with a nitrogen inlet. Then it was heated to 60-80 °C for reaction for 18 h with an initiator ABIN (1 wt%) while being stirred. Finally, the reaction product was added to excess petroleum ether, and the resultant white precipitate was the product polymer MAMA. The reaction of the three copolymers can be given as follows.



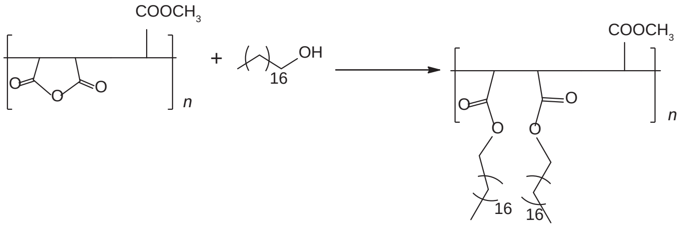
2.4 Preparation of NMAMA

The mixture of MAMA polymers and oleylamine (in a molar ration of 1:2) were dissolved in tetrahydrofuran (THF), and reacted at 20±0.5 °C for 20-32 h under vigorous stirring. Then excess hexane was added in 10:1 volume ratio and a white precipitate (crude product of polymer NMAMA) was obtained. The product was further purified 3 times in an excess THF, and dried under vacuum at 50 °C for 24 h. The reaction of the three copolymers can be given as follows:



2.5 Preparation of OMAMA

The polymer MAMA was added to molten octadecyl alcohol, and reacted at 100-110 °C for 8-12 h under vigorous stirring. Then the reaction product was added to ethanol, and the unreacted octadecyl alcohol was removed by ultrasonic cleaning at 60 °C. Finally, the obtained product was dried under vacuum at 50 °C for 24 h. The reaction of the three copolymers can be given as follows:



2.6 Characterization and analysis of pour point depressants

2.6.1 Infrared spectrum

The sample for infrared spectrum analysis was prepared by the KBr disk method. The infrared spectrum analysis was carried out with a Tensor 27 Fourier transform infrared spectrometer made by Bruker, Germany. The resolution ratio was 4 cm^{-1}, and the number of scans was 64.

2.6.2 Gel chromatography

Gel chromatography analysis was performed with a Waters 2410 Gel permeation chromatograph (GPC) (Waters Company, USA), which was equipped with a Waters 515 system, a 2410 refractive index detector and two styragel gel columns, and calibrated with narrow molecular weight polystyrene standards, to estimate the molecular weights and polydispersity of the synthesized polymers. THF was used as a mobile phase at a flow rate of 1.0 mL/min. The concentrations of polymer samples were in the range of 2.0-3.0 mg/mL, and the injection volume was 50 μL for each analysis. The temperature of columns and detectors was maintained at 35 °C.

2.6.3 Differential scanning calorimetry

The differential scanning calorimetry analysis was conducted with a DSC822e (Mettler Company, Switzerland) at a flow rate of N_2 of 50 mL/min, and the increasing temperature rate of 10 °C /min.

2.6.4 Scanning electron microscopy

The scanning electron microscopy was conducted with a SEM JSM-7600F (JEOL, Japan) at an acceleration voltage of 5-30 kV, and an electron beam current of 10^{-13}-2×10^{-9} A.

2.6.5 Evaluation of pour point depressing

The samples for evaluation of their pour point depressing properties were prepared by a typical standard method (Chen et al, 2010). Polymer was dissolved in xylene to make different concentrations of mother liquor. The mother liquor was added into crude oil (1.5 mL mother liquor per 10 g crude oil), and then the mixture was heated to 45 °C and kept at 45 °C for 30 minutes under vigorous stirring. Using a petroleum product solidifying point tester SYD-510G(Shanghai Changji Chemical Instruments Company, with an accuracy of 0.1 °C), the pour point was determined according to method SY/T0537-2008.

3 Results and discussion

3.1 Structural characterization of pour point depressants

3.1.1 Infrared spectrum

Fig. 2 shows the IR spectrum diagram of MAMA, NMAMA and OMAMA. It can be seen that, for MAMA, the C−H stretching vibrations of methyl and methylene groups appeared at around 2,962 cm^{-1}, and C=O and C−O stretching vibrations of ester groups were at 1,744 cm^{-1} and 1,161 cm^{-1}, respectively. The absorption peaks of maleic anhydride appeared at 1,858 cm^{-1} and 1,789 cm^{-1}. While the absorption near 2,300 cm^{-1} belonging to the initiator disappeared, implying that the initiator was exhausted. It suggests that the two reactants were totally polymerized to the product, MAMA (Zhou, 2000; Zhang, 2006).

For NMAMA (see Fig. 2), the peaks at 2,926 cm^{-1} and 2,866 cm^{-1} were assigned to the C−H stretching vibration of methyl and methylene groups, and the absorption peaks at 1,736 cm^{-1} and 1,168 cm^{-1}were attributed to C=O and C−O stretching vibration. The peaks belonging to MAMA (1,858 cm^{-1} and 1,789 cm^{-1} shown in Fig. 4) disappeared. The characteristic band at 1,568 cm^{-1} was the absorption of C=C stretching vibration of the product introduced by reactant oleylamine. The absorption peaks at 1,062 cm^{-1} and 1,664 cm^{-1} were attributed to the existence of amide. This spectrum showed that oleylamine and MAMA were completely reacted, and polymerized to NMAMA.

For OMAMA (Fig. 2), the bands at 2,921 cm^{-1} and 2,848 cm^{-1} showed the C−H stretching vibration of methyl and methylene groups. The C=O and C−O absorption peaks of the ester appeared at 1,710 cm^{-1} and 1,063 cm^{-1}. The absorptions at 1,858 cm^{-1} and 1,789 cm^{-1} belonging to the anhydride of NMA disappeared, indicating that MAMA was converted to product, and the octadecanol was introduced into OMAMA.

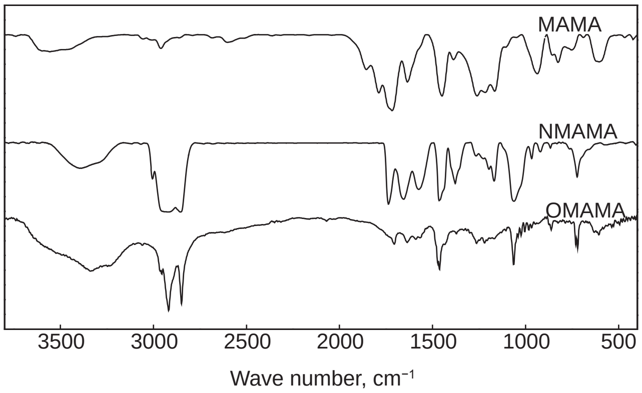


Fig. 2 IR spectrum of MAMA, NMAMA and OMAMA

3.1.2 Gel chromatography

The molecular weights (Mw) of three polymers were all of the order of a hundred thousand, and their dispersancy indexes were in the range of 2.5-2.6. But the molecular weight of OMAMA is smaller than that of NMAMA. Moreover, octadecyl alcohol and oleylamine have almost the same relative molecular weight, indicating that the anhydride ring of NMAMA can be opened and grafted (Hagel, 2011; Kostanyan and Voshkin, 2011).

Table 2 GPC data of the three polymers

Polymers	Number-average molar mass (Mn)	Molecular weight (Mw)	Dispersancy index
MAMA	54769	151126	2.62
OMAMA	78652	203749	2.59
NMAMA	85423	256741	2.50

3.1.3 Differential scanning calorimetry

From the aspect of molecular structure, the glass transition is one relaxation phenomena of the amorphous part of polymers from frozen to plastic condition. At a temperature lower than glass transition temperature (T_g), polymers are frozen and the molecular chains and partial chains are hard to move. Under the same experimental conditions, the main factor influencing T_g is the structure of polymers. The flexibility of polymers depends on the structural property of their main chains, therefore, the polymers with flexible chains corresponds to a low T_g (Sabadini et al, 2010).

The glass transition temperature (T_g) of MAMA is 130 °C. However, the T_g of NMAMA and OMAMA are 115 °C and 50 °C, respectively (see Fig. 3), indicating that the flexibility of OMAMA molecular chains is better than that of NMAMA, attributed to the existence of hydrogen bonds between the carboxyl groups of OMAMA (Hutchinson , 2009).

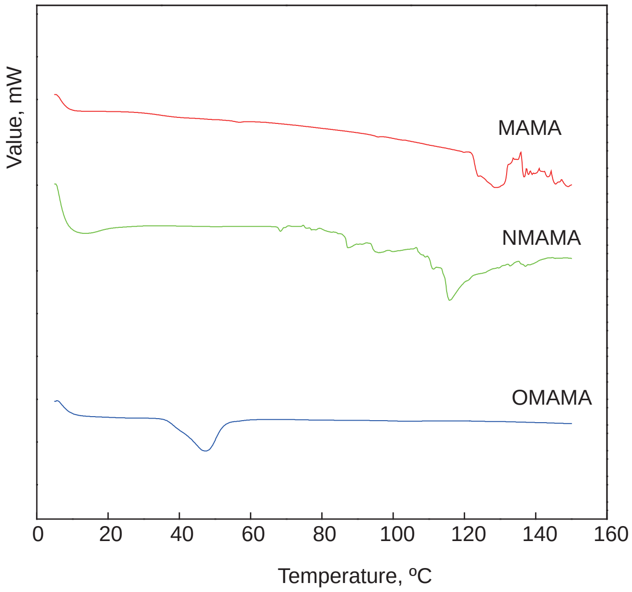


Fig. 3 DSC diagram of MAMA, NMAMA and OMAMA

3.2 Pour point depressing properties and mechanisms of polymers

3.2.1 Molecular dynamical simulation of pour point depressants

In crude oil, the precipitation of paraffin wax is formed through a three-dimensional network structure at low temperature (Yi and Zhang, 2011; Dilawaravk and Srivatavasp, 1994). There exist π bonds among the polymers synthesized in this paper, which are accompanied with intermolecular hydrogen bonds. Because hydrogen bonding interactions are stronger than the van der Waals force, paraffin molecules can be combined more easily with hydrogen bonds. This has an effect on paraffin morphology and the forming process of its network structure, preventing or weakening the formation of three-dimensional network structure (Olayo et al, 2004). As a result, the polymers have excellent pour point depressing properties.

A simulation model was created in a virtual cube box with a 6.0 nm side, comprising 10 comb polymers NMAMA and xylene as solvent molecules. The virtual temperature was set to 303 K, and the Construction tool in Amorphous Cell Tools module was used to build the model. The initial and simulated structures of polymers were compared under the COMPASS force field (Jin et al, 2003; Ilnytskyi et al, 2008).

The micro behavior of comb polymers can be studied through the aggregation structure. As is shown in Fig. 4, system molecules had a certain aggregation after a long dynamic simulation. The main driving force for the aggregation of these compounds was π bonds and hydrogen bonds. Therefore, the properties of polymers' energy were studied during the process of dynamic molecular simulation.

The model was optimized using the Minimize tool, and then the Dynamics tool in the Discover Tools module was used for molecular dynamic calculation. The kinetic parameters were set as follows: NVT system of 303 K, number of steps of 10,000, time step of 1.0 fs, dynamics time of 10.0 ps, frame output every: 50 steps.

The π bonds and hydrogen bonds in polymers affected paraffin morphology and the forming process of network structure, subsequently preventing or weakening the formation of paraffin three-dimensional network structure, so that polymers had fine pour point depressing properties. The molecular dynamical simulation result in Fig. 5 showed that, the potential energy gradually increased to a stable value, however, the non-bond energy was relatively small and did not change significantly.

To sum up, molecules had a certain aggregation after the long dynamic simulation; the potential energy gradually increased to a stable value, and structure became stable. So theoretically the polymers have pour point depressing properties.

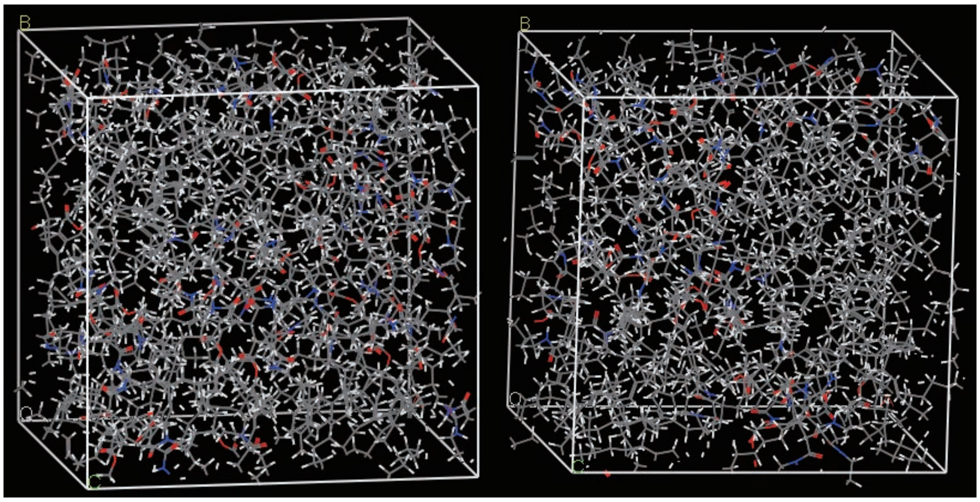


Fig. 4 Initial and simulated structures of comb polymers

3.2.2 Pour point depressing

The crude oil used in experiment was from the Daqing and Jilin oil fields, China. The pressure of the sampled crude oil is 0.26 MPa, the pour point of crude oil is 38 °C, and wax content in crude oil is 29.9%.

Fig. 6 shows the relationship between the concentration

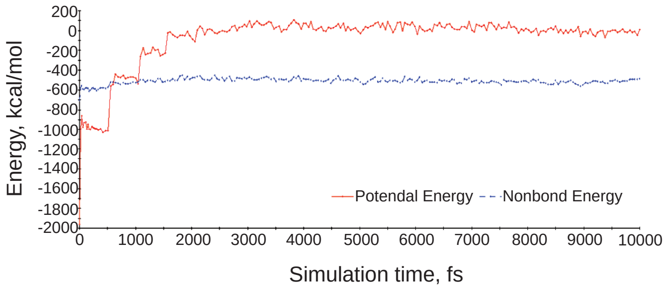


Fig. 5 The change of potential and non-bond energy during molecular dynamical calculation

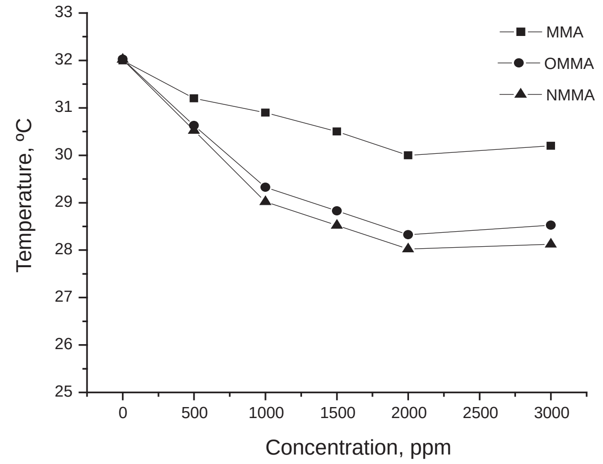


Fig. 6 Oil pour point change with the concentration of polymers

of polymers and the pour point of crude oil. It can be seen that the pour point of crude oil decreased with increasing concentration of the polymers. When the concentration of the polymers was equal to or larger than 2,000 ppm, the pour point temperature of crude oil changed very little. Therefore, the optimal concentration of polymers is 2,000 ppm. The pour point of crude oil was decreased by only 2.0 °C with MAMA, whereas it was decreased by 4.3 °C with NMAMA and OMAMA , showing that the modified polymers NMAMA and OMAMA have significantly better pour point depressant properties.

3.2.3 Pour point depressing mechanisms of polymers

The solubility of polymers can be reduced because of their long side chains, while polymers with short side chains have high solubility that can efficiently prevent the crystallization of paraffin. There are both long side chains and short side chains in the NMAMA and OMAMA structures. If the polymers contain only long carbon chains, under normal circumstances, it will be of a spiral structure and cannot provide attachment points for paraffin crystallization. The combination of short and long chains in a polymer's structure gives it with good solubility in crude oil, as a result, polymers prepared in this work had good pour point depressing effect as crude oil additives even at low temperature.

The π bonds in polymers played two roles. First, it can provide sufficient points for the crystallization. Second, the carboxyl groups and the other side chains can form strong hydrogen bonds, which can reduce the glass transition temperature of the polymers. The hydrogen bonds can provide different attachment points for paraffin crystallization, and guide them to grow in right direction. Thus, paraffin will not crystallize by itself, and not hinder the flowability of crude oil.

The SEM photographs of the three samples (MAMA, NMAMA and OMAMA) are shown in Figs. 7, 8 and 9. The snow-like picture of MAMA indicated the crystallization of paraffin. The pictures of OMAMA and NMAMA were of small-and-uniformly-distributed particles, showing the dispersancy of paraffin crystals had been improved greatly. It suggested that the paraffin grew up in a certain direction when MAMA was added to crude oil. However, when OMAMA or NMAMA was added to crude oil, the paraffin crystals became to be small-and-uniformly distributed particles due to different attachment points, thus preventing paraffin from further crystallization and reducing the pour point of crude oil.

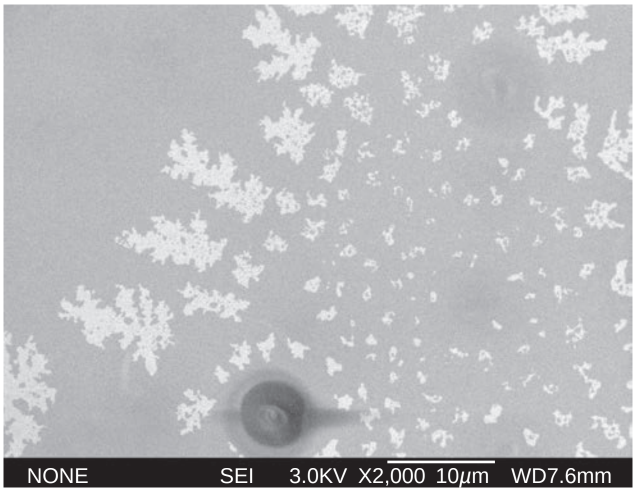


Fig. 7 SEM photograph of MAMA

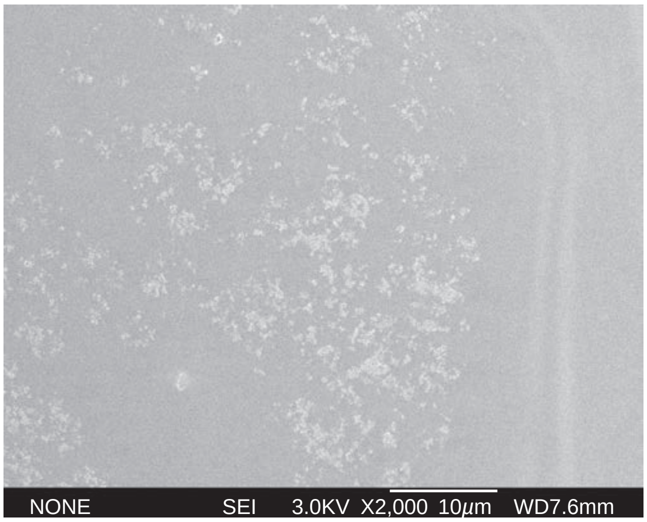


Fig. 8 SEM photograph of NMAMA

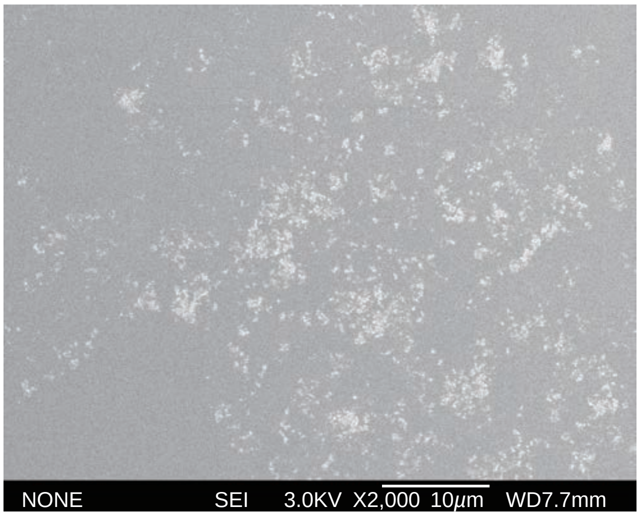


Fig. 9 SEM photograph of OMAMA

4 Conclusions

In this study, two novel comb polymers OMAMA and NMAMA were synthesized by changing the MAMA branches and polar functional groups. Their structures were characterized by IR and GPC. Then the pour point depressing properties and mechanisms of polymers were studied by DSC and SEM. Results show that, besides the molecular weight and concentration of polymers, the length of side chains and the number of functional groups also have obvious influence on the depressing ability. The π bonds and hydrogen bonds in the molecular structures of depressants are the key factors to improve the pour point depressing properties. These results suggest that both OMAMA and NMAMA are potential pour point depressants for industry.

References

Allan L E N, Perry M R and Shaver M P. Organometallic mediated radical polymerization. Progress in Polymer Science. 2012. 37 (1): 125-128

Beristain M F, Jimenez-Solomon M F, Ortega A, et al. Magnetic properties of polymerized diphenyloctatetrayne. Materials Chemistry and Physics. 2012. 136 (2): 1126-1128

Chen W H, Zhao Z C and Yin C Y. The interaction of waxes with pour point depressants. Fuel. 2010(89): 1127-1132

Deshmukh S and Bharambe D. Evaluation of effect of polymeric pour point depressant additives on Indian waxy crude oil. Petroleum Science and Technology. 2009. 27(18): 2096-2098

Dilawaravk and Srivatavasp. Crystallization characteristics of waxes from undoped crude oil. Science and Technology. 1994. 47(4): 150-152

Du T, Wang S, Liu H, et al. The synthesis and characterization of methacrylic acid ester-maleic anhydride copolymer as a lube oil pour point depressant. Petroleum Science and Technology. 2012. 30(2): 210-212

Frauendorfer E and Hergeth W-D. Industrial Polymerization Monitoring. Macromolecular Symposia. 2011. 302(1): 1-5

Galicia J A, Cousin F, Dubois E, et al. Local structure of polymeric ferrogels. Journal of Magnetism and Magnetic Materials. 2011. 323(10): 1210-1215

Hagel L. Gel filtration: Size exclusion chromatography. The Free Encyclopedia. 2011. 54: 50-62

Hutchinson J M. Determination of the glass transition temperature. Journal of Thermal Analysis and Calorimetry. 2009. 98(3): 579-589

Ilnytskyi J, Neher D, Wilson M, et al. Molecular dynamics simulations of various branched polymeric liquid crystals. Molecular Crystals and Liquid Crystals. 2008. 496: 185-190

Janis Hunt. Oil and energy trends: a monthly publication of international energy statistics and analysis. Crude Oil Production. 2012. 37(2): 18-25

Jin Y, Liu W and Gong L. A study of reaction mechanism of the nucleophilic reagent in the cationic polymerization of isobutene with molecular simulation. CHINA ELASTOMERICS. 2003. 13(6): 40-45

Kostanyan A and Voshkin A. Analysis of cyclic liquid chromatography. Theoretical Foundations of Chemical Engineering. 2011. 45(1): 67-72

Lehn J M. Supramolecular chemistry: concepts and perspectives. VCH, Welnhelm. 1995

Mieulet P. A new pour point depressant. World Oil. 1966. 5(10): 95-101

Olayo M G, Cruz G J, Ordoñez E, et al. Molecular simulation of plasma polymerized polyaniline-iodine compounds. Polymer. 2004. 45(10): 3565-3575

Pan Z R. Polymer Chemistry. Beijing: Chemical Industry Press. 2007. 26-44 (in Chinese)

Prahl U. Influence of asphaltenes on the crystallization of paraffins. Erdoel Erdgas Kohle. 2000. 116(2): 95

Sabadini E, Francisco K R and Bouteiller L. Bis-urea-based supramolecular polymer: The first self-assembled drag reducer for hydrocarbon solvents. Langmuir. 2010. 26(3): 1482-1486

Soni H P and Kiranbala. Designing maleic anhydride-α-olifin copolymeric combs as wax crystal growth nucleators. Fuel Processing Technology. 2010(91): 997-1004

Tang X H, Yan S Q and Wang S X. Synthesis of acrylic ester-styrene-maleic anhydride pour point depressant. Journal of Lanzhou University. 2009. 45(1): 69-72 (in Chinese)

Tokuma F, Hiroshi U and Shiro K. Synthesis of ultrahigh molecular weight polyphenols by oxidative coupling. Macromolecules. 2003. 36(22): 8213-8215

Wang D, Zhao X F and Ma Chunxi. Research on high wax crude oil compounds. Advances in Fine Petrochemicals. 2007. (12): 31-34 (in Chinese)

Yang X H. Design and Management of Oil Pipelines. Dongying: China University of Petroleum Press. 2006. 76-155 (in Chinese)

Yi S and Zhang J J. Relationship between waxy crude oil composition and change in the morphology and structure of wax crystals induced by pour-point-depressant beneficiation. Energy & Fuels. 2011. 25(4): 1685-1686

Zhang F Y. Synthesize and characterize of crude oil viscosity reducers. Dissertation for master's degree. Southwest Petroleum University. 2006. 20-42

Zhou F S. The improvement mechanisms of flowability and the preparation and application of copolymeric viscosity reducers for crude oils. Dissertation for Doctor's degree. Xi'an Jiaotong University. 2000. 31-52

Zhu Q L. Study on the reaction of dihydromyrcenol and maleic anhydride. Shandong Chemical Engineering. 2012. 41(1): 8-16 (in Chinese)

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