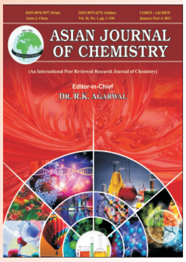
Asian Journal of Chemistry; Vol. 26, No. 19 (2014), 6658-6664

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.17387



Polymerization of C_9 Fraction from Ethylene Cracking Catalyzed by Al^{3+}-Loaded Styrenic Cation Exchange Resin

JINGHUA YANG[1,2], ZUBIN CAO[3] and YUTAI QI[4,5,*]

[1]School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin, P.R. China
[2]Changchun University of Technology, Changchun, P.R. China
[3]College of Petrochemical Technology, Liaoning Shihua University, Fushun, P.R. China
[4]School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin, P.R. China
[5]Sinopec Management Institute, Beijing, P.R. China

*Corresponding author: Tel: +86 13701026068, E-mail: yutaiq123@163.com

Received: 13 February 2014; *Accepted*: 12 May 2014; *Published online*: 16 September 2014; AJC-15982

Studies on the chemical, copolymerization and hydrogenation modification of C_9 petroleum resin are numerous, whereas those on polymerization process, particularly polymerization catalysts, are rare. The current study aimed to explore the catalyst performance of the Al^{3+} ion exchange resin catalyst in petroleum resin polymerization. A gel-type solid resin catalyst used for the polymerization of the ethylene cracking byproduct C_9 (boiling range, 100-200 °C) was prepared by loading anhydrous $AlCl_3$ onto strong acid styrene-type cation exchange resins. The obtained polymerizates were analyzed using an infrared spectrometer. The results showed that the Al^{3+}-loaded styrene-type cation exchange resin resulted in the absence of elution liquids produced from the reaction system, circumventing the process of catalyst removal. The softening point of the obtained petroleum resin product was higher than the softening point of petroleum resin directly catalyzed by anhydrous $AlCl_3$.

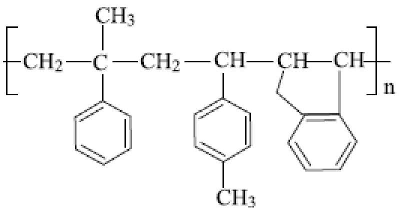
Keywords: C_9 fraction, Polyene polymerization, FTIR analysis, Cation exchange resin.

INTRODUCTION

More than 75 % of the starting materials of the ethylene cracking unit are derived from light diesel fuel. The byproducts of cracking include the C_5, C_6 -C_8 and C_9 fractions and fractions greater than C_{10}. In the C_9 fraction, there were more than 150 components and this number increases or decreases with changes in the feedstock, cracking and cracking depth. From a synthetic point of view, the components can be divided into two categories[1,2]: active components that can be polymerized, such as styrene, vinyl toluene and dicyclopentadiene and non-active components, such as benzene and polycyclic aromatic hydrocarbons. The C_9 by-products from the ethylene unit had complex constituents with similar boiling points, making fine separation difficult. Although not suitable for separation, C_9 serves as an excellent polymeric material because it contains large quantities of vinyl and polycyclic aromatic hydrocarbons[3-5]. Among the various techniques for C_9 petroleum resin synthesis, catalytic polymerization with a Lewis acid catalyst has been most extensively utilized for its fast reaction speed and mild reaction conditions. Polymerization by $AlCl_3$ is the most widely used in literature.

The catalytic polymerization of C_9 petroleum resin has the advantages of low reaction temperature, high speed, low energy consumption, easy operation and high yields, but the softening point of the product is low and hydrocarbon oil emulsification can easily occur during washing or alkali washing. The product treatment is problematic. The equipment corrodes badly and environmental pollution is generated[6,7]. With the market demand for higher product quality, investigations into optimal conditions for multi-stage polymerization and the development of pollution-free and efficient polymerization catalysts have become major tasks in the industry of petroleum resin synthesis.

C_9 petroleum resin polymerization is catalyzed *via* cationic polymerization of mainly olefin monomers at temperatures below 100 °C, in the presence of a catalyst. The formation of a carbenium ion activity center causes chain polymerization (generally including chain initiation, chain growth, chain transfer and chain termination reactions), ultimately producing synthetic petroleum resin. The infrared spectrum of C_9 petroleum resin molecular chain structure and ^{1}H NMR analyses show that C_9 petroleum resin is a weakly polar substance with molecular chains primarily composed of styrene (*o*-, *m*-, *p*-), methyl styrene, dicyclopentadiene, indene and methyl indene[5,8,9]. The simulated molecular formula is as follows:


(1)

In the polymerization of C_9, the catalyst type and catalyst form have a substantial impact on the properties of the synthesized C_9 petroleum resin. The softening point of the resin is an important service index and is related not only to the polymer structure but also to its molecular weight[10]. The more active units are oriented in a straight chain molecule of petroleum resin and the greater the molecular weight, the higher the softening point of the petroleum resin is. In the catalytic polymerization of C_9 petroleum resin, $AlCl_3$ is widely applied because cationic polymerization reactions initiated by $AlCl_3$ are more likely to produce polymers with high molecular weight[1,7]. However, it is difficult in practice to use dry powder $AlCl_3$ directly. The consumption is increased because dry powder $AlCl_3$ agglomerates easily in reaction liquid. In addition, dry powder $AlCl_3$ is unevenly distributed in the polymerization system, which decreases the polymer softening point[9,10]. For this reason, researchers have tried many alternatives, such as developing a liquid form of $AlCl_3$,[11], but the compound must be removed from the catalyst after reaction termination. This process requires alkali washing and water washing, which causes oil emulsion polymerization and thus affects the resin quality. Alkali washing and water washing also produce wastewater containing the catalyst, which causes environmental pollution. To address the above problems, the researchers have loaded $AlCl_3$ onto carriers such as activated carbon and SiO_2 to make solid acid catalysts for the polymerization of C_9 petroleum resin[12,13]. Although many researchers have reported the copolymerization modification and hydrogenation modification of C_9 petroleum resin[5,14], petroleum resin solid catalysts have rarely been reported. In our opinion, if there is no high-quality polymeric precursor of C_9 petroleum resin, neither copolymerization modification nor hydrogenation modification will produce good results. The development of an efficient catalytic polymerization catalyst is the key to a fundamentally improved C_9 petroleum resin polymerization process. Additionally, as environmental protection draws more and more attention, the development of environmentally friendly catalysts[15,16] and catalyst carriers is likewise receiving greater attention.

Styrenic strong-acid cation exchange resin not only serves as the catalyst for esterification and etherification reactions but can also be used as a carrier, which is made into a solid super acid by ion exchange to load metal ions or transition metal ions. This solid super acid can be used for olefin polymerization[17]. Many researchers have performed a multitude of studies on cation exchange resins that load other ions[18-24]. We selected a large exchange-capacity styrene-type strong acid cation exchange resin for Al^{3+} loading through ion exchange to create a solid catalyst[25-27] and then used it for C_9 polymerization. At the end of the reaction, the catalyst was directly filtered and separated, avoiding the washing process. Infrared analysis was used to determine the products' functional groups. The softening points of the products obtained by the solid catalyst and the products obtained directly using the $AlCl_3$ catalyst were compared to examine the effect of the solid catalyst on polymerization. Solid catalyst recycling experiments were also performed.

EXPERIMENTAL

Preparation of solid catalysts of Al^{3+} styrene-type cation exchange resin: The materials included anhydrous $AlCl_3$ (AR; Beijing Guohua, China), carbon tetrachloride (99 %; Shenyang Xinxi, China), 732 strong acid styrene cation exchange resin (Na type: complete exchange capacity, ≥ 4.50 mmol/g; effective grain size, 0.40-0.60 mm; post-attrition sphericity, ≥ 90 %) (Tianjin Ruijinte, China), hydrochloric acid (37.5 % concentration), ethanol (≥ 99 %) and deionized water.

Catalyst loading: The 732 strong acid styrene-type cation exchange resin was treated with a 7 % hydrochloric acid solution, replacing the Na counterions with protons. The H-type resin was washed with deionized water until it reached neutral pH, then dried under reduced pressure for 12 h. The dried cation exchange resin was placed into a four-necked 1000 mL bottle containing a recycling and stirring device for 2-4 h of swelling with carbon tetrachloride solution. Anhydrous aluminum trichloride was slowly added until the mass ratio between the anhydrous aluminum trichloride and the cation exchange resin was 1:1 for a 10 h exchange at 76 °C. The loaded cation exchange resin was then slowly poured into deionized water for filtration. The obtained resin was washed three times with ethanol and then dried for no less than 20 h under normal pressure (12 h under reduced pressure). The amount of Al^{3+} loaded onto the resin was determined by EDTA complexometric titration.

Determination of the content of Al^{3+} by EDTA complexometric titration: The amount of Al^{3+} loaded onto the resin was determined by the EDTA back titration method as follows:

Preparation: The materials included pH 5 acetic acid-sodium acetate buffer solution, pH 10 ammonia-ammonium chloride buffer solution, 0.05 M EDTA standard solution (disodium ethylenediamine tetraacetate) and 0.05 M zinc standard solution.

Calibration of standard EDTA solution concentration: Benchmark ZnO that ignited to a constant weight at 800 °C was weighed accurately (1 g) and Eriochrome Black T indicator was obtained. Blank experiments were performed on both at the same time. At the end of calibration, the solution changed from purple to blue by EDTA titration. After loading, 4 g of resin was accurately weighed (precise to 0.0002 g). The resin was soaked in 20 mL of 10 % nitric acid for 24 h. The resulting solution was transferred to a 250 mL volumetric flask. The platinum dish was washed several times and the solution in the 250 mL volumetric flask was diluted of to volume and shaken. Twenty-five milliliters of the solution was accurately moved to a 500 mL conical flask and diluted with water to 100 mL. Twenty milliliters of EDTA standard solution and

2 drops of dimethyl orange indicator were carefully added to the solution. Ammonia was added until the solution turned purple red (1:1) and then hydrochloric acid was added until it was barely yellow (1:1). The solution was boiled for 3 min, then cooled to room temperature and 25 mL acetic acid sodium acetate buffer and 2 drops of two methyl phenol orange indicator were added. The solution was titrated with a standard solution of 0.05 M ZnO and changed from yellow to pale yellow (no recorded reading). One gram of NH_4F solid was added and the solution was heated to boiling. The ZnO standard solution was used to titrate the solution until it changed from yellow to pale yellow. The volume of ZnO standard solution consumption, V_1 (mL) was recorded. The Al^{3+} content was calculated by eqn. 2:

$$Al^{3+}(g/l) \equiv \frac{MV_1 \cdot 26.98}{V} \qquad (2)$$

In the formula: M-moles of ZnO standard solution

V_1-Volume of ZnO standard solution consumption V_1 (mL)

V-Volume of the sample (mL)

26.98-Molecular weight of Al

Influence of different conditions on loading of Al^{3+}: The loading conditions were studied according to a published method[26]. The mass ratio of $AlCl_3$ and the cation exchange resin was 1.1:1. The cation exchange resin was swelled with solvent for 2 h. The exchange reaction temperature varied with the boiling points of the solvents. The reaction time was 10 h. EDTA complexometric titration was used to analyze the Al^{3+} content. The influence of different solvents and different washing methods on the loading of Al^{3+} was tested and the results are given in Tables 1 and 2.

TABLE-1
INFLUENCES OF DIFFERENT SOLVENTS ON THE LOADING OF Al^{3+}

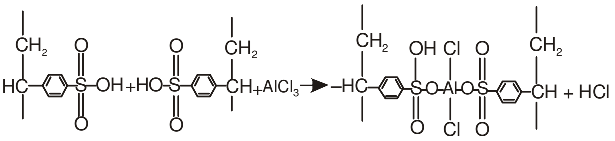
Solvent	Toluene	Ethanol	Carbon disulfide	Carbon tetrachloride
Al^{3+} % (w)	1.14	1.60	2.01	2.21

TABLE-2
INFLUENCES OF DIFFERENT WASHING METHODS ON THE LOADING OF Al^{3+}

Washing method	Al^{3+} % (w)
Water	0.89
Water-ethanol-water	2.21
Water-carbon tetrachloride-ethanol-water	1.79
Water-acetone-isopropyl alcohol-ethyl ether-water	2.29
Acetone-isopropyl alcohol-ethyl ether-water	2.52

Based on the experimental methods as well as the properties and sources of the reagents reported in Tables 1 and 2, carbon tetrachloride was selected as the solvent. Water-ethanol-water was adopted as the post-treatment. The temperature was 76 °C and the exchange time was 10 h. A solid acid catalyst of styrene-type cation exchange resin was prepared. The Al^{3+} loading content was 2.21 %.

Infrared spectra of Al^{3+}-loaded styrene-type cation exchange resins: The combination of anhydrous $AlCl_3$ and the cation exchange resin in a nonpolar solvent allowed the fixation of Al^{3+} onto the surface of the resin to form a solid acid catalyst based on the following formula:



(3)

Structural analyses of the cation exchange resin were performed before and after Al^{3+} loading with a Nicolet 6700 infrared spectrometer (Thermo Electron, USA) and a KBr pellet. The results are shown in Fig. 1.

As shown in Fig. 1, the Al^{3+} -loaded styrene-type cation exchange resins exhibited no variation in the 1247-1188 cm^{-1} region and a small variation in the 1008-834 cm^{-1} region, which showed that the sulfonic acid group on the exchange resin was charged. This process showed that there was a reaction between $AlCl_3$ and the cation exchange resin, *i.e.*, Al^{3+} was loaded into the cation exchange resin.

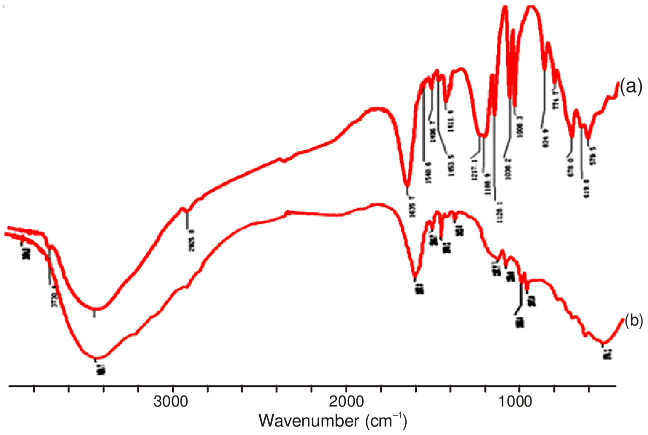


Fig. 1. Infrared spectra of the cation exchange resins (a) before and (b) after Al^{3+} loading

Polymerization of C_9 catalyzed by Al^{3+}-loaded styrenic cation exchange resin: C_9 fraction (boiling range, 100-200 °C; density, 0.9207 g/cm^3; the Ethylene Plant of Jilin Petrochemical Corporation, China). Toluene (99.5 %; Shenyang Xinhua, China). Four-necked bottle with round bottom (1000 mL, device thermometer, condenser, mechanical stirrer). Vacuum distillation unit (500 mL distillation flask; 500 mL control electric heating jacket, Beijing Zhongke Aobo Technology Co. Ltd). Water ring vacuum pump (model: SHZ-D (III, specifications: 15 l, limit pressure: 0.098 MPa, Honghua instrument industry and Trade Co., Ltd. of Gongyi City). Softening point tester (SYD-2806D; temperature measurement range: 5-125 °C; accuracy of temperature 0.1 °C; heating rate (5 ± 0.5 °C/min). The heating rate was controlled by PIC and fuzzy logic algorithm. Magnetic stirring was employed. The steel ball properties were 3.5 ± 0.05 g with 9.53 mm diameter and a JTJ052-2000 standard ring. The heating medium was glycerol.

Polymerization of the C_9 fraction: We compared the cation exchange resin-catalyzed polymerization of the C_9 fraction with the $AlCl_3$-catalyzed polymerization of the C_9 fraction. For polymerization with the cation exchange resin, the dried loaded cation exchange resin catalyst (based on the content of Al^{3+}), the raw materials (150 g) and toluene (as the polymerization solvent, such that the volume ratio of toluene to the raw material was 2:5) were placed into the four-necked bottle and the temperature was maintained at 50 °C. After the reaction, the Al^{3+}-loaded cation exchange resin catalyst was filtered and the polymer solution underwent reduced-pressure distillation at 0.098 MPa. For polymerization with the $AlCl_3$ catalyst, $AlCl_3$ was first dissolved in toluene (the volume ratio of toluene to the raw material was 2:5) in the four-necked bottle. 150 g raw material was dropped into the solution at a speed of 2 drops per second. Polymerization took place when the temperature was increased to the polymerization temperature after dripping. After a certain period of time, the terminator (20 mL methanol) was added and the reaction was stirred for 0.5 h. Then, 10 % NaOH was added, followed by 0.5 h of stirring. The washing procedure was conducted. The polymer solution removed from the catalyst underwent pressure distillation and the petroleum resin was obtained. The softening point was determined to show the difference between the two polymerization methods. An infrared spectrometer was used for structural analysis of the polymerization product catalyzed by the Al^{3+}-loaded styrenic cation exchange resin.

Softening point measuring method: A ball of a known weight was placed inside a sample disk within a specified size metal ring. The softening point of the petroleum resin was determined by heating the sample at a rate of 5 ± 0.5 °C/min until the sample decreased by 25.4 mm. The difference between the results of two repeated measurements was not more than 2 °C.

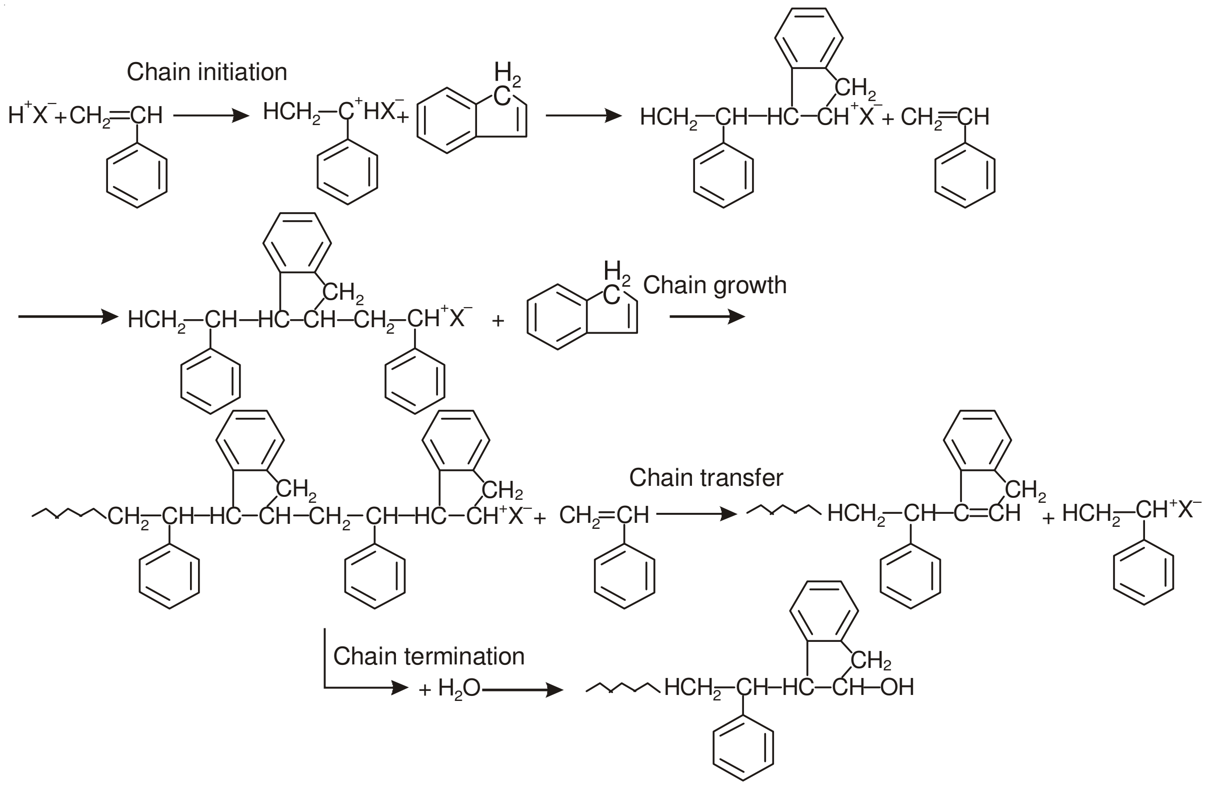
Reproducibility: The difference in the test results obtained by two laboratories for the same sample was not more than 5.5 °C.

RESULTS AND DISCUSSION

A catalyzed polymerization reaction generally includes chain initiation, chain propagation, chain transfer and chain termination reactions. The reaction mechanism is given by the following equation:

A previous paper mentioned the splitting decomposition of the secondary product C_9 petroleum resin of ethylene, which has a molecular chain formed by styrene (*o*-, *m*-, *p*-), *p*-methylstyrene, dicyclopentadiene, indene and methyl indene as the main structural unit and is a very weak material. The chain propagation reaction is the key step of polymerization and directly affects the softening point of the resulting petroleum resin. If a straight chain polymer is formed during polymerization, as illustrated by eqn. 1, the softening point is relatively high, but if a substitution reaction occurs on the benzene ring or a hetero-crosslinked product of the polymer occurs during the polymerization reaction, the softening point is low. The polymerization reaction is exothermic[28], and if it is not well controlled, the heat of the reaction will cause local overheating and formation of the gel polymer, which can also result in a low softening point. In addition, a low softening point of the petroleum resin can be caused by using the anhydrous $AlCl_3$-catalyzed polymerization reaction directly, as $AlCl_3$ can easily lead to alkylation and eliminate the secondary reaction of the β-proton[29], resulting in chain termination and chain transfer and thus in more small-molecule polymers. By using the anhydrous $AlCl_3$ ion exchange polymerization catalyst, however, the Al^{3+} is immobilized in the styrene cation exchange resin, which effectively reduces the implosion compared to directly mixing anhydrous $AlCl_3$ and concentrates the cationic polymerization active centers, promoting the chain reaction. When the reaction is completed, the product can be directly separated by filtration, without alkali washing, water washing, or adding any other inorganic materials to the polymerization system.

Influence of catalyst dosage on the softening point and yield of the petroleum resin: Using the Al^{3+} exchange resin catalyst and the $AlCl_3$ catalyst directly, with a polymerization time of 6 h, the influence of catalyst dosage on the softening



(4)

point and the rate of petroleum resin formation is shown in Figs. 2 and 3.

Figs. 2 and 3 show that the yield of petroleum resin and the softening point are both maximized when the catalyst amount is 2.5 %. Furthermore, the above two figures show the same dosage of Al^{3+} cation exchange resin catalyst can provide a higher yield and higher softening point than the $AlCl_3$ catalyst. The reason may be that mixing with the $AlCl_3$ catalyst causes a higher probability of collisions between the cations and other ions, which can cause chain termination and chain transfer reactions and form many small-molecule polymers. In addition, the nucleophilic $AlCl_3$ catalyst[28] can promote side reactions of alkylation and form a cross-linked product or colloid, which lowers the softening point of the petroleum resin. The polymerization reaction with the Al^{3+} exchange resin catalyst is different. Cationic polymerization is initiated by the solid catalyst when olefin molecules first adsorb on the surface of the resin and then form cations. The olefin in the polymerizable liquid has more opportunities to contact cations, which encourages the chain reaction to produce a polymer whose opposite strand is relatively large. Therefore, using Al^{3+} exchange resin as the catalyst can produce a higher yield and softening point than using the $AlCl_3$ catalyst directly. Figs. 2 and 3 show that no matter what catalyst is used in the catalytic polymerization, when the dosage of catalyst is more than 2.5 %, both the softening point of the petroleum resin and the yield are decreased because the chain transfer and chain termination reactions increase as the amount of the catalyst and the active center increase.

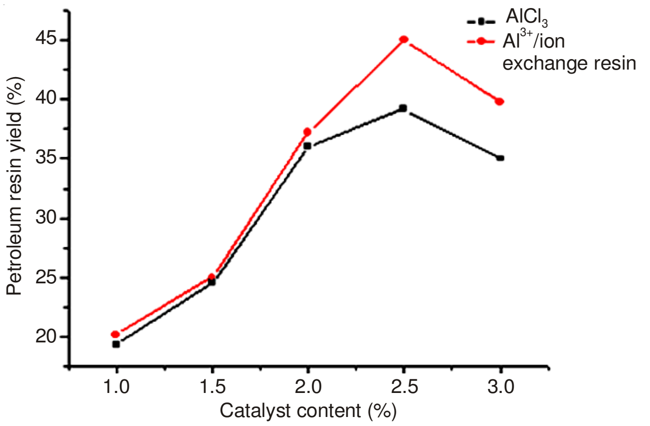


Fig. 2. Influence of catalyst dosage on the yield of petroleum resin. Reaction conditions: $AlCl_3$, polymerization temperature 40 °C; Al^{3+}/ion exchange resin catalyst polymerization temperature, 50 °C

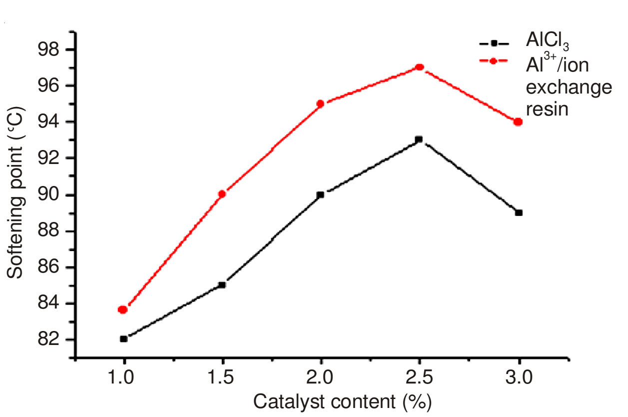


Fig. 3. Influence of catalyst dosage on the softening point of petroleum resin. Reaction conditions: $AlCl_3$, polymerization temperature 40 °C; Al^{3+}/ion exchange resin catalyst polymerization temperature, 50 °C

Influence of temperature on the softening point and yield of petroleum resin: The Al^{3+} exchange resin catalyst and the $AlCl_3$ catalyst were used at a dosage of 2.5 %. The polymerization time was 6 h. The influence of temperature on the softening point and the yield of petroleum resin is shown in Figs. 4 and 5.

Figs. 4 and 5 show that, in the distillate polymerization of C_9 using $AlCl_3$ as the catalyst, the yield and softening point are maximized at 40 °C. Using Al^{3+} exchange resin catalyst, a higher temperature is required to reach the maximum yield and the highest softening point compared with using $AlCl_3$. The reason may be that when the $AlCl_3$ catalyst is used directly, the initial cationic polymerization velocity is fast and olefin polymerization reaction is exothermic[28], which increases the polymerization rate. When the temperature continues to increase, due to the effect of nucleophilic $AlCl_3$[29], the rate of substitution in or on the benzene ring increases, leading to crosslinked polymers and lowering the softening point of the resin. There is little chance for these side reactions using Al^{3+}/cation exchange resin catalyst in the catalytic polymerization reaction, so the decrease in the softening point is caused by

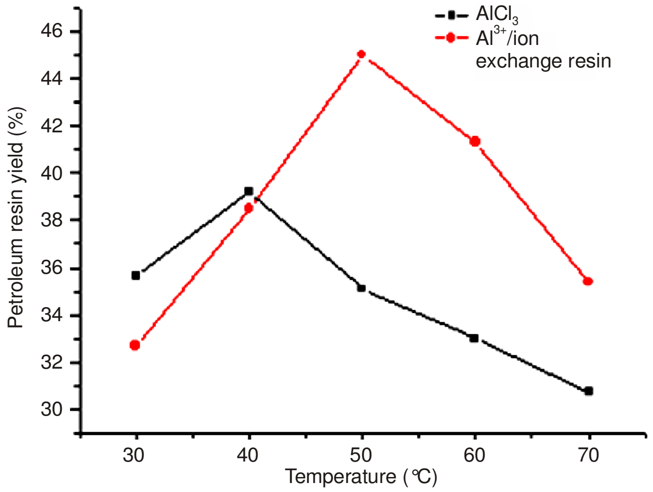


Fig. 4. Influence of temperature on the yield of petroleum resin

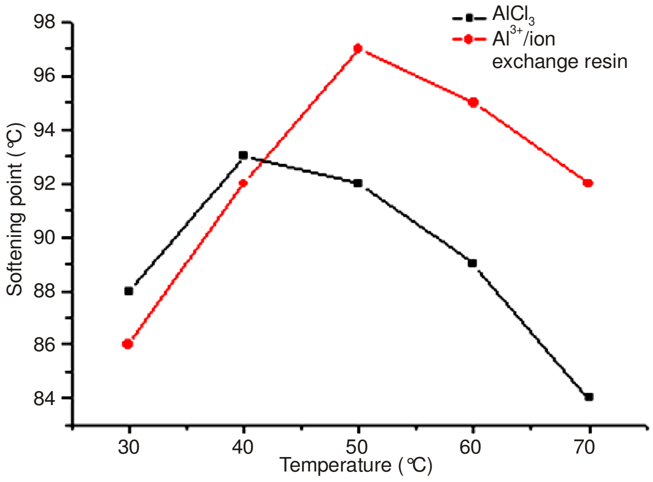


Fig. 5. Influence of temperature on the softening point of petroleum resin

accelerating the reaction rate, which encourages the formation of small-molecule chains. After the temperature reaches 50 °C, continued heating will increase the speed with which the catalyst initiates cationic polymerization, but the reaction rate becomes faster, increasing the chain transfer and chain termination reactions and leading to the formation of small-molecule chain polymers, again decreasing the yield of petroleum resin and lowering the softening point.

Influence of polymerization time on the softening point and yield of petroleum resins: The Al^{3+} exchange resin catalyst and the $AlCl_3$ catalyst were used. The dosage was 2.5 %. The polymerization time was 6 h. The influence of time on the softening point and the yield of petroleum resin is shown in Figs. 6 and 7.

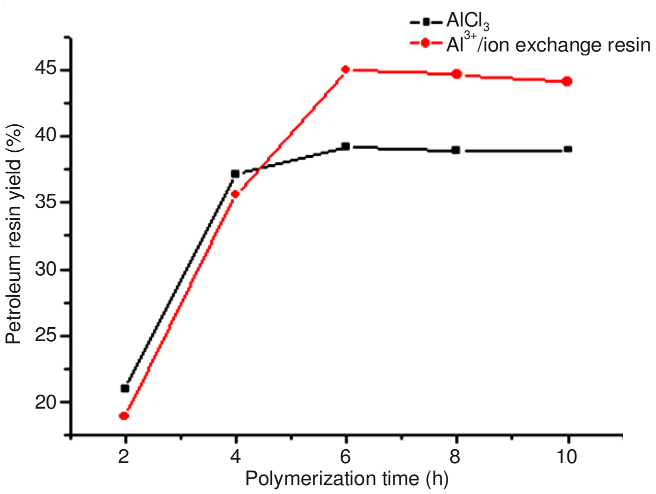


Fig. 6. Influence of polymerization time on the yield of petroleum resin. Reaction conditions: Polymerization temperature for $AlCl_3$, 40 °C; polymerization temperature for Al^{3+} cation exchange resin catalyst, 50 °C

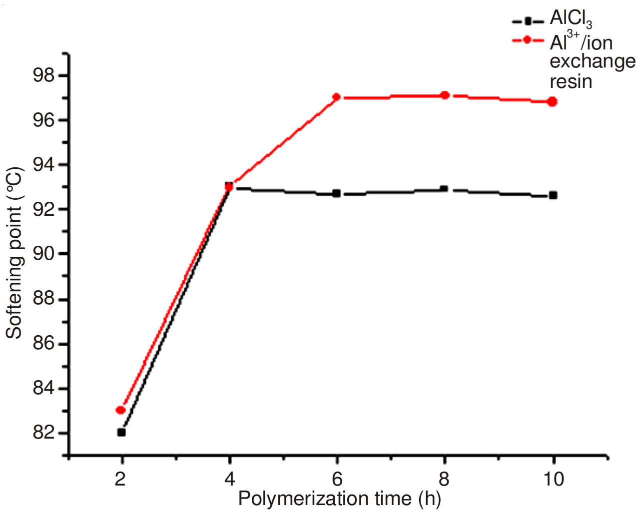


Fig. 7. Influence of polymerization time on the softening point. Reaction conditions: Polymerization temperature for $AlCl_3$, 40 °C; polymerization temperature for Al^{3+} cation exchange resin catalyst, 50 °C

The two catalysts require different lengths of time to reach the highest yield in the polymerization reaction. There is no obvious change in the petroleum resin softening point after 4 h of polymerization using the $AlCl_3$ catalyst directly, but when using the Al^{3+} cation exchange resin as the polymerization catalyst, the yield and softening point are both maximized at 6 h. There is no significant change after 6 h in either yield or softening point. Because of the different mixing conditions of the catalysts, the active centers formed initiate cationic polymerization at different speeds. The reaction rate using the $AlCl_3$ catalyst directly is faster than the reaction rate using the Al^{3+} ion exchange resin[13].

The yield and softening point of petroleum resin from the C_9 fraction preparation are both higher when using the Al^{3+} cation exchange resin catalyst than when using the $AlCl_3$ catalyst directly. Although two more hours are required for the polymerization to terminate than when using the $AlCl_3$ catalyst, the yield and softening point of the petroleum resin are high and at the end of polymerization, the catalyst and the polymerization solution can be separated by filtration. Avoiding the water wash can also improve the quality of the petroleum resin. This result is consistent with the use of a solid acid catalyst for catalytic polymerization[12,13], namely that a catalyst with a carrier for $AlCl_3$ can initiate olefin chain polymerization well and obtain a polymer with a high softening point. Of course, because of the limited reliability under such experimental conditions, we only tested the effect of a single factor. To further demonstrate the excellent catalytic performance of the Al^{3+} cation exchange resin catalyst in C_9 petroleum resin synthesis, we analyzed the two infrared spectra of petroleum resin products.

Petroleum resin structure analysis: Infrared analysis of C_9 petroleum resin. A Nicolet 6700 infrared spectrometer (FTIR) (Thermo Electron, Thermo Company) with a KBr tablet was used to analyze the petroleum resin structure. The IR spectrum is shown in Fig. 8.

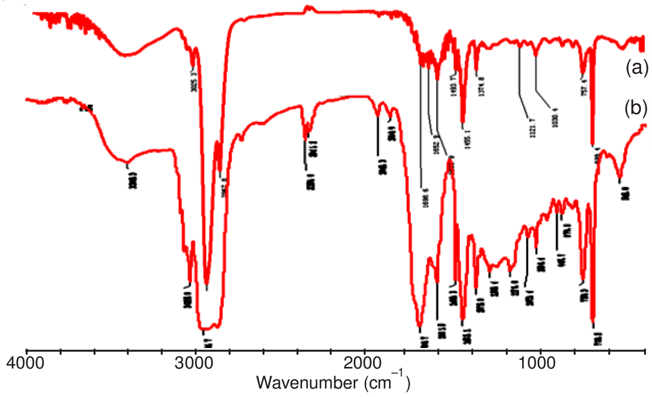


Fig. 8. Infrared spectra of petroleum resin. (a), catalyzed by $AlCl_3$. (b), catalyzed by Al^{3+}/ion exchange resin. Reaction conditions for (a) and (b): Temperature, 50 °C; catalyst amount, 2.5 % (calculated based on the content of Al^{3+}); reaction time, 6 h

In the IR spectrum, organic compounds show a CH stretching vibration absorption in the region of 3300-2800 cm^{-1} with 3000 cm^{-1} as a bound. A band above 3000 cm^{-1} is an unsaturated carbon-CH stretching vibration absorption, which can appear for alkene, alkyne and aromatic compounds, while a band below than 3000 cm^{-1} is generally a saturated CH stretching vibration absorption. If there is an absorption band slightly above 3000 cm^{-1}, the analysis should check for the stretching vibration of unsaturated carbon bond absorption peaks in the frequency region 2250-1450 cm^{-1}: alkenyl, 1680-1640 cm^{-1}; and aromatic rings, 1600, 1580, 1500, 1450 cm^{-1}. From Fig. 8a, b, in the IR spectrum of the C_9 petroleum resin, absorption peaks exist on both sides of 3000 cm^{-1}, indicating that there is no unsaturated CH or saturated CH stretching vibration and that the aromatic ring exists in the polymer at 1601, 1453 cm^{-1}. This result is consistent with the report showing that the molecular chain of C_9 petroleum resin is a weakly polar substance containing styrene-(*o*-, *m*-, *p*-), *p*-methylstyrene, dicyclopen-tadiene, indene and methyl indene as the main structural unit. Fig. 8 shows that the peak of product b is different from the peak of product a. At 3000 cm^{-1}, the widened peak on both sides of the polymer chain shows an increase in the structural units of unsaturated CH and saturated CH. The peaks at 1601, 1453 cm^{-1} for product b are wider and higher than the peaks for product a, which indicates that with the b catalyst, the aromatic polymer units increased. The above analysis shows that using the Al^{3+} cation exchange resin catalyst can produce a higher softening point, which illustrates the use of the Al^{3+} cation exchange resin catalyst to obtain a petroleum resin with a long molecular chain.

In this study, we first used comparative experiments and qualitative analysis of the petroleum resin product to verify the utility of the Al^{3+} cation exchange resin catalyst for the polymerization of olefins in complex multi-material systems. The qualitative analysis of the experimental results preliminarily illustrates that it is practical to use an Al^{3+} cation exchange resin catalyst for the polymerization of C_9 petroleum resin. To further examine whether Al^{3+} cation exchange resin has good catalytic performance in the polymerization of C_9 petroleum resin, in the next experiment, we used on-line gas chromatography to test the change in the olefin monomer. We combined this information with polymer molecular weight measurements by the thermogravimetric analysis for qualitative and quantitative analysis of the polymer.

Conclusion

Many researchers have studied the use of an immobilized solid $AlCl_3$ catalyst to simplify and improve the polymerization process and the quality of petroleum resin produced using the secondary product C_9 fraction. We employed styrene cation exchange resin as a carrier and loaded $AlCl_3$ on the ion exchange resin to create an Al^{3+} solid ion exchange resin catalyst. This catalyst obtains good catalytic activity for polymerization in the olefin synthesis of a multi-component complex C_9 petroleum resin. Styrene cation exchange resin is an environmentally friendly green catalyst carrier, low-cost and easy to obtain.

In this experiment, the maximum petroleum resin yield obtained using the solid catalyst was 45 %, with a softening point up to 97 °C. This polymerization reaction achieves the best results under atmospheric pressure, 50 °C and 6 h of polymerization. Using infrared analysis to compare the experiments and products, we determined that the solid catalyst has good catalytic activity for polymerization.

Solid catalysts using cation exchange resin as a carrier to load metal ions are widely used in esterification, etherification and other reactions. We plan to use the proposed catalyst as the polyene component for polymerization and continue to study the reaction mechanism of the C_9 fraction of complex multi-component systems with an Al^{3+} cation exchange resin solid catalyst to provide richer data on the catalytic polymerization mechanism of ion exchange.

ACKNOWLEDGEMENTS

The authors thank the staff of the Analysis Center for their careful direction and the colleagues for their assistance during the experiment.

REFERENCES

1. F. Zongyan, *Petrochem. Ind. Technol.*, **13**, 49 (2006).
2. W. Yinglong, *J. Qingdao Univ. Sci. Technol.*, **24**, 65 (2003).
3. Shell Oil Company, US Patent 5212285, (1993).
4. Chu Guang Xing Chan Ltd, CN Patent 1726231 (2006).
5. Y. Lujun, J. Dahao, X. Jiao, M. Lei and L. Xiaonian, *Petrochem. Ind. Technol.*, **41**, 1181 (2012).
6. L. Lanfen, *Qilu Petrochem. Technol.*, **32**, 76 (2004).
7. H. Kai, *Guangdong Petrochem.Technol.*, **39**, 89 (2012).
8. P. Gaocong, L. Baotian, X. Shaoji *et al.*, *Coatings Ind.*, **1**, 39 (1998).
9. Y. Lei, W. Shubin and X. Binglian, *Guangdong Petrochem. Technol.*, **35**, 56 (2007).
10. P. Gaocong, L. Baotian, X. Shaoji, *et al.*, *Thermal Decomp. Mechanism Dynamics*, **3**, 10 (1997).
11. Z. Qinghuan, W. Yulan, Y. Weizou, *et al.*, *J. Daqing Petroleum Institute*, **19**, 59 (1995).
12. B. Keqiang, Z. Zhibing, D. Fulong *et al.*, *Petrochem. Ind. Technol.*, **25**, 270 (1996).
13. Z. Dongming, X. Songlin, W. Baohe *et al.*, *Ind. Catal.*, **4**, 35 (1997).
14. H. Junzuo and Z. Shisen, *Chinese Polym. Bull.*, **4**, 62 (2010).
15. M.J. Climent, A. Corma and S. Iborra, *RSC Adv.*, **2**, 16 (2012).
16. D. Kumar, D.N. Kommi, R. Chebolu, S.K. Garg, R. Kumar and A.K. Chakraborti, *RSC Adv.*, **3**, 91 (2012).
17. F. Xinliang, G. Chuanjin and Z. Chengxue, *Chinese J. Org. Chem.*, **23**, 1348 (2003).
18. T. Matsuura, K. Ohnaka, M. Takagi, M. Ohashi, K. Mibu and A. Yuchi, *Anal. Chem.*, **80**, 9666 (2008).
19. I.H. Rhee and D.A. Dzombak, *Langmuir*, **15**, 6875 (1999).
20. B. Saha and M. Streat, *Ind. Eng. Chem. Res.*, **44**, 8671 (2005).
21. G. Gelbard, *Ind. Eng. Chem. Res.*, **44**, 8468 (2005).
22. T. Zhang, L. Yang, Z. Zhu and J. Wu, *Mol. Catal.*, **18**, 315 (2002).
23. W. Min, C. Wenyi, M. Jun and W. Haiyan, *J. Petrochem. Univ.*, **17**, 24 (2004).
24. S.D. Alexandratos, *Ind. Eng. Chem. Res.*, **48**, 388 (2009).
25. J. Tiihonen, M. Laatikainen, I. Markkanen and E. Paatero, *Ind. Eng. Chem. Res.*, **38**, 4832 (1999).
26. L. Fuan, Z. Junxiu and H. Huamin, *J. Catal.*, **12**, 394 (1991).
27. P. Botella and A. Corma, *Appl. Catal.*, **203**, 253 (2000).
28. L. Shixiong, Petroleum Refing Engineering, Petroleum Industry Press, Beijing, China (2009).
29. A. Kanazawa, S. Shibutani, N. Yoshinari, T. Konno, S. Kanaoka and S. Aoshima, *Macromol.*, **45**, 7749 (2012).