Preparation of C₅ Petroleum Resins Using Et₃NHCl-AlCl₃ as Catalyst

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The cationic polymerization of C₅ refinery stream with ionic liquid (Et₃NHCl-AlCl₃) as catalyst was reported in this paper. Effects of polymerization conditions on the softening point and colour were investigated. M_n and α_H of resins produced in toluene and chloroform were favourably comparable. It was found that resins produced in chloroform had a higher softening point (105 °C). Et₃NHCl-AlCl₃ catalyst improved the colour of resin compared with AlCl₃. The optimum reaction conditions for this reaction are as follows: solvent: CHCl₃; m(Et₃NHCl-AlCl₃) = 2.6579 g; X(AlCl₃) = 0.69; T = 45 °C. The use of Et₃NHCl-AlCl₃ as catalyst promises to afford easy catalyst recovery by simple phase separation while being less corrosive, easier to handle and minimising process waste water production.

Key Words: Cationic polymerization, C₅ refinery stream, Ionic liquid.

INTRODUCTION

Petroleum resins are well known and produced by the Friedel-Crafts polymerization of various feeds, which may be pure monomer feeds or refinery streams containing mixtures of various unsaturated materials. The resulting hydrocarbon resins can range from viscous liquids to hard, brittle solids with colours ranging from water white to pale yellow amber, or dark brown depending on the monomers used and the specific reaction conditions. The lighter the resins, the wider the application scope of the polymerization of resins. Typically, pure monomer resins tend to be water white. C₅ monomer resins tend to be yellow. Hydrocarbon resins are widely used in adhesives, rubbers, hot-melt coatings, printing inks, paint, flooring, road marking and polymer and other applications. The resins are usually used to modify other materials¹.

Generally speaking, the purer the feed, the easier it is to polymerize. For example, pure or concentrated 1,3-pentadiene (PD) is easier to polymerize than a C₅ refinery stream dose. Pure monomers are, however, more expensive to produce than the refinery streams which are often by-products of the cracked petroleum. 1,3-Pentadiene in C₅ refinery stream is the primary reactive component².

C₅ refinery stream-based polymers produced through cationic polymerization are commonly prepared in the presence of various Lewis acids (such as BF₃, complexes of BF₃, AlCl₃, or alkyl aluminium chlorides)^{3,4}. Although these Lewis acids are of high activity and relatively low cost, their separation from the reaction system is difficult and the reuse/disposal of

the catalysts is a greater challenge to industry, as large volumes of acidic aluminum waste is created^{5,6}. Sometimes the resin appears poor colour.

The ionic liquids based on complex salts consisting of an inorganic anion such as Al₂Cl₇⁻ and an organic cation like *n*-alkyl substituted pyridinium ion are among the most interesting systems. The advantages of such ionic liquids are as follows: (1) They are quite stable and remain in the liquid state in a wide temperature range. (2) They are more tolerant to water and other protolytic compounds as compared, for instance, with AlCl₃. (3) The ionic liquids can be easily separated from the reaction mixture containing a hydrocarbon substrate. (4) They can be used repeatedly without significant deactivation. Finally, ionic liquids serve as highly ionic media with strong polarization properties⁷. Ionic liquids have been successfully employed as catalyst for polymerization^{8,9}, esterification¹⁰, alkylation¹¹ and Beckmann rearrangement¹². To our best of knowledge no papers have been published on the cationic polymerization of C₅ petroleum resins catalyzed by Et₃NHCl-AlCl₃.

As Et₃NHCl-AlCl₃ is not soluble in solvents (CHCl₃ and toluene), the after-treatment of the catalysts and products from the reaction systems is easy by simple phase separation. This paper reported the cationic polymerization of C₅ refinery stream using Et₃NHCl-AlCl₃ as catalyst.

EXPERIMENTAL

Toluene (Aldrich) was distilled over CaH₂ under reduced pressure. AlCl₃ (Aldrich) was purified by sublimation under

argon atmosphere. Et_3NHCl (Aldrich) is used without further purification. Chloroform (Aldrich) was distilled twice from CaH_2 under an inert atmosphere. C_5 refinery streams were purchased from Shanghai research institute of petrochemical technology. The component are shown in Table-1. It is used without further purification.

TABLE-1
Composition of C_5 refinery stream

Component	W (%)
cis-1,3-Pentadiene	21.16
trans-1,3-Pentadiene	37.66
Cyclopentene	31.94
Cyclopentane	9.13
Others	0.11

Preparation of C_5 hydrocarbon resins: The Et_3NHCl - AlCl_3 catalyst were prepared according to the literature¹³.

The polymerization was carried out in a three-neck-reactor equipped with Teflon magnet in a dry nitrogen atmosphere. Et_3NHCl - AlCl_3 and 100 mL solvent were introduced into the reactor. The polymerization was achieved by introduction of 100 mL C_5 refinery stream by syringe. After the required time, ionic liquid was separated from the system by simple phase separation. The polymerization was quenched by adding a small amount of methanol. The resulting resin solution was washed with 10 mL water. The unreacted material, solvent and low-molecular weight oligomers were removed by steam-stripping at 250 °C.

Softening point: Ring and ball method ASTM D 3461 was used for determination of the softening point of resins.

Resin colour: Resin colour was determined *via* the Gardner method: a 50 % solution of resin in toluene is compared with a set of standard colour disks.

Yield: The yield of the resin was calculated as follows: $\text{yield} = m_p/m_r \times 100\%$, m_p : weight of product, m_r : weight of raw material.

Cyclization degree(α_H): ^1H spectra were recorded on a Bruker Avance 400 MHz in deuterated chloroform or methylene chloride. The proton relative unsaturation loss per monomer unit (α_H) calculated by ^1H NMR (in CDCl_3) was defined as the difference between the theoretical unsaturation degree (equal to 25 % of the total of protons, assuming negligible the ratio of 3,4-units) and the experimental unsaturation degree [$d_{\text{exp}} = a/(a+b)$] divided by the theoretical unsaturation degree: $\alpha_H = (0.25 - d_{\text{exp}})/0.25$. a is the peak area of the olefinic protons and b is the integration of the peaks of the aliphatic protons (Fig. 1).

Molecular weight: The molecular weight of the polymers were determined by size exclusion chromatography (SEC) in tetrahydrofuran on a chromatograph equipped with three polystyrene gel columns (PL gel). Number-average molecular weight was calculated on the basis of a polystyrene calibration.

RESULTS AND DISCUSSION

Investigation of the polymerization conditions on the properties of resin product

Polymerization temperature: In order to investigate the importance of polymerization temperature, the polymerizations were performed at various temperatures. The results are shown

Fig. 1. ^1H NMR spectrum of the resin

shown in Table-2. It can be seen that the molecular weight decreased with increasing temperature. Because the higher the polymerization temperature, the faster the chain transfer reaction, the lower the molecular weight.

Table-2 also shows that α_H increased with increasing temperature. When polymerization temperature was 55 °C, it was found that α_H decreased greatly due to the formation of other byproducts. More cyclizations occurred at high temperature (45 °C). It was shown that α_H was greater in polar solvent. This result was assigned to the formation of more dissociated active species.

TABLE-2
POLYMERIZATION OF C_5 REFINERY STREAM
AT VARIOUS TEMPERATURES^a

Run	Solvent	Temp. (°C)	Yield (%)	$\overline{M}_n$ (g/mol)	α_H	Softening point (°C)	Gardner colour
1	Toluene	-5	6.0	5289	0.5096	32	4
2	Toluene	5	8.5	5200	0.5108	38	4
3	Toluene	15	17.1	5102	0.5592	42	4
4	Toluene	25	32.6	4805	0.5641	44	4
5	Toluene	35	42.3	4606	0.5899	50	4
6	Toluene	45	50.1	4236	0.6404	51	4
7	Toluene	55	58.3	3993	0.6317	47	4
8	CHCl_3	-5	16.2	6628	0.5486	67	3
9	CHCl_3	5	26.5	6536	0.5519	72	3
10	CHCl_3	15	35.7	6368	0.5823	86	3
11	CHCl_3	25	46.8	6290	0.6075	92	3
12	CHCl_3	35	51.2	4926	0.6303	94	3
13	CHCl_3	45	58.7	4705	0.6918	105	3
14	CHCl_3	55	58.8	4638	0.6800	103	3

^a $m(\text{Et}_3\text{NHCl-AlCl}_3) = 2.6579\text{g}$; $X(\text{AlCl}_3)$: 0.69; reaction time: 4 h

When the polymerization carried out in toluene and chloroform at 45 °C, the molecular weight in toluene was lower than in chloroform, which was mainly due to the occurrence of chain transfer reaction in toluene¹⁴. This result was confirmed by ^1H NMR analysis of the precipitate of the polymers in CDCl_3 (Fig. 2). The analysis showed that toluene acted as a chain transfer agent in the reaction ($\delta = 2.31$ ppm; $\delta = 7.07$ ppm).

Fig. 2. ¹H NMR spectra of the polymers in toluene

In order to obtain a higher softening point product, it is preferable to operate the polymerization in polar solvent at 45 °C. The softening point is related to the molecular weight and α_H . With increasing the molecular weight and α_H , the softening point increased. When polymerization temperature was 45 °C, a maximum softening point (105 °C) was achieved. When polymerization temperature was higher than 45 °C, it was observed that the softening point decreased.

Mole fractions of AlCl₃ in Et₃NHCl-AlCl₃: The effects of the mole fractions of AlCl₃ in Et₃NHCl-AlCl₃ on C₅ refinery stream polymerization were investigated and the results are shown in Table-3. The Lewis acidity of Et₃NHCl-AlCl₃ varied as the mole fraction of AlCl₃ in Et₃NHCl-AlCl₃ [X(AlCl₃)] varied. When the ionic liquid was basic [X(AlCl₃) < 0.50], there was no product. Ionic liquid generates initiating species under acidic conditions. With increasing the acidity of ionic liquid, the activity of ionic liquid increased, so did the yield. When the mole fraction of AlCl₃ varied from 0.50 to 0.69, the molecular weight and yield increased. After that molecular weight decreased, which was mainly due to the high activity of ionic liquid that results in the occurrence of irreversible termination and chain transfer reactions.

In toluene, when the mole fraction of AlCl₃ varied from 0.60 to 0.67, the molecular weight and α_H increased greatly, but increased slightly in chloroform.

Amount of Et₃NHCl-AlCl₃: Table-4 shows the influence of amounts of Et₃NHCl-AlCl₃ (X(AlCl₃) = 0.69) on polymerization. It can be concluded that increasing the amount of Et₃NHCl-AlCl₃ led to an increase of the yield. As shown in Table-4, the highest softening point of 105 °C was obtained when m(Et₃NHCl-AlCl₃) was 2.5679 g.

Reaction time: Fig. 3 shows the influence of reaction time on the yield. It is clearly observed that a longer reaction time favours the reactions with higher yield. Fig. 3 also shows that the yield is greater in CHCl₃ than in toluene at the same reaction time. When the reaction time was 4 h and the reaction solvent was CHCl₃, the yield was nearly 60 %.

TABLE-3
POLYMERIZATION OF C₅ REFINERY STREAM AT VARIOUS MOLE FRACTIONS OF ALUMINIUM CHLORIDE IN Et₃NHCl-AlCl₃^b

Run	Solvent	X (AlCl ₃)	Yield (%)	$\overline{M}_n$ (g/mol)	α_H	Softening point (°C)	Gardner colour
1	Toluene	0.40	0	-	-	-	-
2	Toluene	0.50	0	-	-	-	-
3	Toluene	0.60	47.2	4079	0.5566	25	4
4	Toluene	0.67	49.3	4167	0.6316	43	4
5	Toluene	0.69	50.1	4236	0.6404	51	4
6	Toluene	0.71	53.2	4015	0.6318	48	4
7	CHCl ₃	0.40	0	-	-	-	-
8	CHCl ₃	0.50	0	-	-	-	-
9	CHCl ₃	0.60	58.1	4458	0.6633	76	3
10	CHCl ₃	0.67	58.5	4557	0.6797	92	3
11	CHCl ₃	0.69	58.7	4705	0.6918	105	3
12	CHCl ₃	0.71	58.8	4666	0.6364	79	3

^bm(Et₃NHCl-AlCl₃) = 2.6579 g; T = 45 °C; reaction time: 4 h

TABLE-4
EFFECT OF AMOUNTS OF Et₃NHCl-AlCl₃ ON POLYMERIZATION^c

Run	m(Et ₃ NHCl-AlCl ₃) (g)	Yield (%)	$\overline{M}_n$ (g/mol)	α_H	Softening point (°C)	Gardner colour
1	1.2839	26.6	4659	0.6856	100	3
2	2.5679	58.7	4705	0.6918	105	3
3	5.1358	58.8	3965	0.6826	93	3

^cT = 45 °C; solvent: CHCl₃; X(AlCl₃) = 0.69; reaction time: 4 h

Fig. 3. Effect of reaction time on the yield of resin

Comparison between the properties of resins produced by AlCl₃ and Et₃NHCl-AlCl₃: The comparison between the resins produced by AlCl₃ and Et₃NHCl-AlCl₃ is listed in Table-5. The softening point of resins produced with Et₃NHCl-AlCl₃ as catalyst was a little lower than with AlCl₃. While the colour of resin was remarkably improved compared with AlCl₃'s.

Conclusion

1. Et₃NHCl-AlCl₃ is an excellent catalyst for the cationic polymerization of C₅ refinery stream.

2. The optimum reaction conditions for this reaction are as follows: solvent: CHCl₃; m(Et₃NHCl-AlCl₃) = 2.6579 g; X(AlCl₃) = 0.69; T = 45 °C; reaction time: 4 h. The softening

TABLE-5
COMPARISON BETWEEN THE RESINS PRODUCED
BY AlCl_3 AND $\text{Et}_3\text{NHCl-AlCl}_3^d$

Run	Catalyst	Temp. (°C)	Yield (%)	$\overline{M}_n$ (g/mol)	α_H	Softening point (°C)	Gardner colour
1	AlCl_3	35	56.2	6218	0.6454	96	6
2	AlCl_3	45	58.6	4026	0.7239	110	6
3	$\text{Et}_3\text{NHCl-AlCl}_3$	35	51.2	4926	0.6303	94	3
4	$\text{Et}_3\text{NHCl-AlCl}_3$	45	58.7	4705	0.6918	105	3

^dSolvent: CHCl_3 ; $X(\text{AlCl}_3) = 0.69$; reaction time: 4 h

point of the resin is 105 °C. and the colour is Gardner 3. The yield is nearly 60 %.

3. The softening point of resin produced with the ionic liquid catalyst is a little lower than with AlCl_3 . While the colour of resin is greatly improved.

4. The use of $\text{Et}_3\text{NHCl-AlCl}_3$ as catalyst promises to afford easy catalyst recovery by simple phase separation. This process can be less corrosive, easier to handle and minimising industrial waste water production.

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