Preparation of C$_5$ Petroleum Resins Using Et$_3$NHCl-AlCl$_3$ as Catalyst

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The cationic polymerization of C$_5$ refinery stream with ionic liquid (Et$_3$NHCl-AlCl$_3$) 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 ºC). Et$_3$NHCl-AlCl$_3$ catalyst improved the colour of resin comparied with AlCl$_3$. The optimum reaction conditions for this reaction are as follows: solvent: CHCl$_3$; m(Et$_3$NHCl-AlCl$_3$)= 2.6579 g; X(AlCl$_3$) = 0.69; T = 45 ºC. The use of Et$_3$NHCl-AlCl$_3$ 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, C$_5$ 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. C$_5$ 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 materials[1].

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 C$_5$ 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 C$_5$ refinery stream is the primary reactive component[2].

C$_5$ refinery stream-based polymers produced through cationic polymerization are commonly prepared in the presence of various Lewis acids(such as BF$_3$, complexes of BF$_3$, AlCl$_3$, 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 Al$_2$Cl$_7^-$ 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 AlCl$_3$. (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 properties[7]. Ionic liquids have been successfully employed as catalyst for polymerization[8,9], esterification[10], alkylation[11] and Beckmann rearrangement[12]. To our best of knowledge no papers have been published on the cationic polymerization of C$_5$ petroleum resins catalyzed by Et$_3$NHCl-AlCl$_3$.

As Et$_3$NHCl-AlCl$_3$ is not soluble in solvents (CHCl$_3$ 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 C$_5$ refinery stream using Et$_3$NHCl-AlCl$_3$ as catalyst.

EXPERIMENTAL

Toluene (Aldrich) was distilled over CaH$_2$ under reduced pressure. AlC1$_3$ (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-l. 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 literature[13].

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 ºC.

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: 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_{exp} = a/(a+b)] divided by the theoretical unsaturation degree: α_H = $(0.25-d_{exp})/0.25$. 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 poly-styrene gel columns (PL gel). Number-average molecular weight was calculated on the basis of a polystyrene calibration.

RESULTS AND DISCUSSION

Invesitation 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
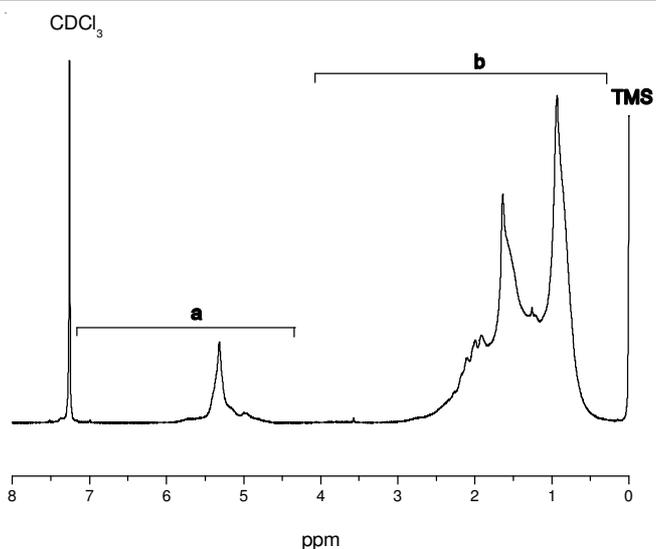

Fig. 1. ^1H NMR spectrum of the resin

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.
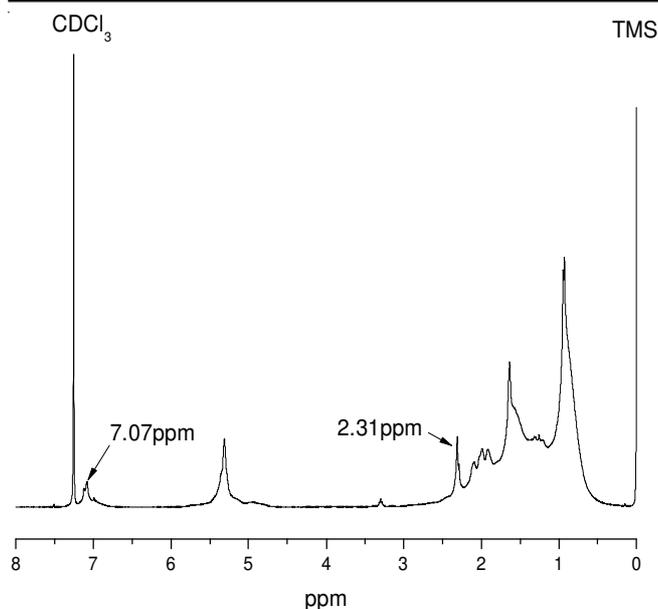
Table-2 also shows that α_H increased with increasing temperature. When polymerization temperature was 55 ºC, it was found that α_H decreased greatly due to the formation of other byproducts. More cyclizations occurred at high temperature (45 ºC). It was shown that α_H was greater in polar solvent. This 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. (ºC)	Yield (%)	$\overline{M_n}$ (g/mol)	α_H	Softening point (ºC)	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(Et_3NHCl-$AlCl_3$) = 2.6579g; X($AlCl_3$): 0.69; reaction time: 4 h

When the polymerization carried out in toluene and chloroform at 45 ºC, the molecular weight in toluene was lower than in chloroform, which was mainly due to the occurrence of chain transfer reaction in toluene[14]. 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 (δ = 2.31 ppm; δ = 7.07 ppm).

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

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

Run	Solvent	X (AlCl₃)	Yield (%)	$\overline{M_n}$ (g/mol)	α_H	Softening point (ºC)	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	CHCl₃	0.40	0	-	-	-	-
8	CHCl₃	0.50	0	-	-	-	-
9	CHCl₃	0.60	58.1	4458	0.6633	76	3
10	CHCl₃	0.67	58.5	4557	0.6797	92	3
11	CHCl₃	0.69	58.7	4705	0.6918	105	3
12	CHCl₃	0.71	58.8	4666	0.6364	79	3

[b]m (Et₃NHCl-AlCl₃) = 2.6579g; T= 45 ºC; reaction time: 4 h

TABLE-4
EFFECT OF AMOUNTS OF Et₃NHCl-AlCl₃ ON
POLYMERIZATION[c]

Run	m(Et₃NHCl-AlCl₃) (g)	Yield (%)	$\overline{M_n}$ (g/mol)	α_H	Softening point (ºC)	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

[c]T = 45 ºC; solvent: CHCl₃; X(AlCl₃): 0.69; reaction time: 4 h

In order to obtain a higher softening point product, it is preferable to operate the polymerization in polar solvent at 45 ºC. 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 ºC, a maximum softening point (105 ºC) was achieved. When polymerization temperature was higher than 45 ºC, 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 is 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 generate 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 occurance 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 ºC 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 %.
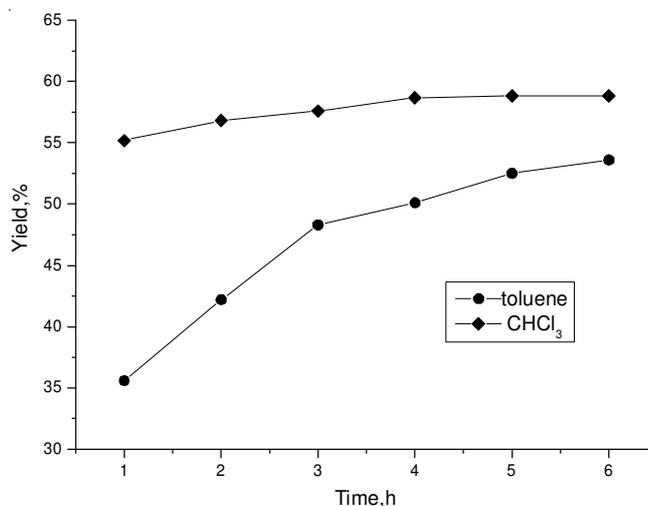

Fig. 3. Effect of reaction time on the yield of resin

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) = 2.6579g; X(AlCl₃) = 0.69; T = 45 ºC; reaction time: 4 h. The softening

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

Run	Catalyst	Temp. (ºC)	Yield (%)	$\overline{M}_n$ (g/mol)	α_H	Softening point (ºC)	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	Et$_3$NHCl-AlCl$_3$	35	51.2	4926	0.6303	94	3
4	Et$_3$NHCl-AlCl$_3$	45	58.7	4705	0.6918	105	3

^{d}Solvent: CHCl$_3$; X(AlCl$_3$) = 0.69; reaction time: 4 h

point of the resin is 105 ºC. 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 Et$_3$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.

REFERENCES

1. K. Lewtas, M.L. Garcia, J.H. Clark and K. Wilson, Petroleum Resins and Their Production with BF$_3$ Catalyst, US Patent 6867267 (2005).
2. J.K. Shorrock, J.H. Clark, K. Wilson and J. Chisem, *Org. Process Res. Dev.*, **5**, 249 (2001).
3. F. Duchemin, V. Bennevault Celton, H. Cheradame, C. Merienne and A. Macedo, *Macromolecules*, **31**, 7627 (1998).
4. J. Santarella, E. Rousset, S. Randriamahefa, A. Macedo and H. Cheradame, *Eur. Polym. J.*, **36**, 2715 (2000).
5. J.H. Clark and D.J. Macquarrie, *Chem. Commun.*, 853 (1998).
6. J.H. Clark and C.N. Rhodes, Clean Synthesis Using Porous Inorganic Solid Catalysts and Supported Reagents; Royal Society of Chemistry, Cambridge (2000).
7. V.A. Ksenofontov, T.V. Vasina, Y.E. Zubarev and L.M. Kustov, *React. Kinet. Catal. Lett.*, **80**, 329 (2003).
8. S.W. Liu, C.X. Xie, S.T. Yu and F.S. Liu, *Catal. Commun.*, **9**, 2030 (2008).
9. S.W. Liu, C.X. Xie, S.T. Yu, M. Xian and F.S. Liu, *Chin. J. Catal.*, **30**, 401 (2009).
10. Y. Zhao, J. Long, F. Deng, X. Liu, Z. Li, C. Xia and J. Peng, *Catal. Commun.*, **10**, 732 (2009).
11. S. Tang, A.M. Scurto and B. Subramaniam, *J. Catal.*, **268**, 732 (2009).
12. S. Guo, Z.Y. Du, S.G. Zhang, D.M. Li, Z.P. Li and Y.Q. Deng, *Green Chem.*, **8**, 296 (2006).
13. K.R. Sherif, L.J. Shyu and C.C. Greco, Linear Alkylbenzene Formation Using Low Temperature Ionic Liquid, US Patent 5824832 (1998).
14. Y.X. Peng, J.L. Liu, L.R. Cun and H.S. Dai, *Polym. Bull.*, **35**, 393 (1995).