

## Cationic Copolymerization of Styrene and C<sub>5</sub> Refinery Stream with Et<sub>3</sub>NHCl-AlCl<sub>3</sub> as Catalyst

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The cationic copolymerization of styrene and C<sub>5</sub> refinery stream with ionic liquid (Et<sub>3</sub>NHCl-AlCl<sub>3</sub>) as catalyst was reported in this paper. Effects of polymerization conditions on the softening point and colour were investigated. Et<sub>3</sub>NHCl-AlCl<sub>3</sub> catalyst improved the colour of resin compared with AlCl<sub>3</sub> and minimising process waste water production. The use of styrene futher improved the colour of resin. The optimum reaction conditions for this reaction are as follows: w<sub>styrene</sub> = 20 %; solvent: CHCl<sub>3</sub>; m(Et<sub>3</sub>NHCl-AlCl<sub>3</sub>) = 2.6579 g; X(AlCl<sub>3</sub>) = 0.69; T = -5 °C.

**Key Words:** Styrene, Ionic liquid, Light colour.

### INTRODUCTION

C<sub>5</sub> petroleum resins are low-molecular weight, thermo-plastic materials that can be produced *via* the cationic polymerization of cracked petroleum distillates using a Friedel-Crafts initiator. They may be used in the fabrication of adhesives, road-markings, printing inks, paints and flooring. They can range from viscous liquids to hard, brittle solids and have colours ranging from water-white to dark brown depending on the monomers used and the specific reaction conditions<sup>1</sup>. Such C<sub>5</sub> refinery streams contain polymerizable monomers such as 1,3-pentadiene. The cationic polymerization of 1,3-pentadiene was initiated by various Lewis acids<sup>2-6</sup>. 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<sup>7,8</sup>. Sometimes the resin appears poor colour.

In order to decrease the colour of resin, solve the separation of catalyst and reduce corrosive waste, we have reported the cationic copolymerization of styrene and C<sub>5</sub> refinery streams with Et<sub>3</sub>NHCl-AlCl<sub>3</sub> as catalyst. In order to further decrease the colour of the resin, the paper reports the cationic copolymerization of styrene and C<sub>5</sub> refinery streams with Et<sub>3</sub>NHCl-AlCl<sub>3</sub> as catalyst.

### EXPERIMENTAL

Styrene (Aladdin), microcrystalline wax (Aladdin), ethylene vinyl acetate copolymer (EVA) (Aladdin), AlCl<sub>3</sub>

(Aldrich) was purified by sublimation under argon atmosphere. Et<sub>3</sub>NHCl (Aldrich) was used without further purification. Chloroform (Aldrich) was distilled twice from CaH<sub>2</sub> under an inert atmosphere. C<sub>5</sub> refinery streams were purchased from Shanghai research institute of petrochemical technology. The component are shown in Table-1. It was used without further purification.

TABLE-1  
COMPOSITION OF C<sub>5</sub> REFINERY STREAM

Component	w (%)
<i>cis</i> -1,3-Pentadiene	21.16
<i>trans</i> -1,3-Pentadiene	37.66
Cyclopentene	31.94
Cyclopentane	9.13
Others	0.11

**Preparation of C<sub>5</sub> hydrocarbon resins:** The Et<sub>3</sub>NHCl-AlCl<sub>3</sub> catalyst were prepared according to literature<sup>9</sup>.

The polymerization was carried out in a three-neck-reactor equipped with teflon magnet in a dry nitrogen atmosphere. Et<sub>3</sub>NHCl-AlCl<sub>3</sub> and 100 mL solvent were introduced into the reactor. The polymerization was achieved by introduction of the mixture (C<sub>5</sub> refinery stream and styrene) 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: yield =  $m_p/m_r \times 100$  %.  $m_p$ : weight of product,  $m_r$ : weight of raw material.

**Cyclization degree ( $\alpha_H$ ) of 1,3-pentadiene segment in copolymer:** <sup>1</sup>H spectra were recorded on a Bruker Avance 400 MHz. The proton relative unsaturation loss per monomer unit ( $\alpha_H$ ) calculated by <sup>1</sup>H NMR 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 [dexp =  $a/(a + b)$ ] divided by the theoretical unsaturation degree:  $\alpha_H = (0.25 - \text{dexp})/0.25$ .  $a$  is the peak area of the olefinic protons and  $b$  is the integration of the peaks of the aliphatic protons.

**W<sub>styrene</sub> in copolymer:**  $w_{\text{styrene}}$  in copolymer were calculated by <sup>1</sup>H NMR.

## RESULTS AND DISCUSSION

### Investigation of the polymerization conditions on the properties of copolymer

**Raw material composition:** The effects of raw material composition on polymerization were investigated. The results are shown in Table-1. When polymerization temperature was 55 °C, the softening point first decreased and then slightly increased with increasing the amount of styrene. Because the chain transfer reaction between styrene and polymer chain was easy to occur at high temperature. The yield increased from 58.8 to 62.6 % with increasing the amount of styrene.

When polymerization temperature was -5 °C, the yield increased from 16.2 to 63.9 % because 1,3-pentadiene is hard to homopolymerize, but can copolymerize with styrene at -5 °C. The softening point increased from 67 to 95 °C with increasing the amount of styrene because the activity of styrene was higher than 1,3-pentadiene at -5 °C. The colour of copolymer became lighter gradually with increasing the amount of styrene. When  $w_{\text{styrene}}$  was 20 %, the colour of copolymer was Gardner-1.

Table-2 also shows that  $\alpha_H$  increased with increasing the amount of styrene at -5 and 55 °C. When polymerization temperature was 55 °C, it was found that  $\alpha_H$  decreased greatly due

to the formation of other byproducts. More cyclizations occurred at high temperature (55 °C). It was shown that  $\alpha_H$  was greater at high temperature. This result was assigned to the formation of more dissociated active species.

Fig. 1 shows that the effects of  $w_{\text{styrene}}$  in raw material on  $w_{\text{styrene}}$  in copolymer. The  $w_{\text{styrene}}$  in copolymer increased with  $w_{\text{styrene}}$  in raw material increased at 55 °C and -5 °C. When the  $w_{\text{styrene}}$  in raw material was same, the  $w_{\text{styrene}}$  in copolymer at 55 °C was higher than at -5 °C.

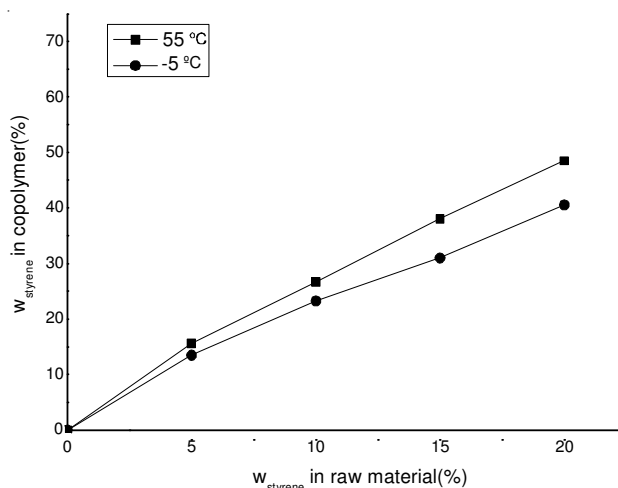


Fig. 1. Effects of  $w_{\text{styrene}}$  in raw material on  $w_{\text{styrene}}$  in copolymer

**Solvent composition:** Table-3 shows the influence of solvent composition on polymerization. It can be concluded that increasing the amount of CHCl<sub>3</sub> led to an increase of the yield. As shown in Table-3, the softening point and  $\alpha_H$  increased with increasing the amount of CHCl<sub>3</sub>. The highest softening point of 95 °C was obtained when the solvent was CHCl<sub>3</sub>.

Run	V(CHCl <sub>3</sub> )/V(CCl <sub>4</sub> )	Yield (%)		Softening point (°C)	Gardner colour	$\alpha_H$
		Soluble polymer	Crosslinked product			
1	0:1	36.6	10.6	87	1	0.6123
2	1:1	40.8	8.9	89	1	0.6496
3	1:0	65.6	-	95	1	0.6513

<sup>b</sup> $w_{\text{styrene}} = 20$  %; T = -5 °C;  $m(\text{Et}_3\text{NHCl-AlCl}_3) = 2.6579$  g;  $X(\text{AlCl}_3) = 0.69$ ; reaction time: 4 h

Run	T (°C)	$w_{\text{styrene}}$ (%)	Yield (%)	Softening point (°C)	Gardner colour	$\alpha_H$
1	55	0	58.8	103	3	0.6800
2	55	5	60.2	83	3	0.6842
3	55	10	61.5	84	3	0.6966
4	55	15	61.9	84	3	0.7430
5	55	20	62.6	85	3	0.7551
6	-5	0	16.2	67	3	0.5486
7	-5	5	36.5	83	3	0.5921
8	-5	10	43.5	85	2	0.6056
9	-5	15	46.8	92	2	0.6446
10	-5	20	63.9	95	1	0.6513

<sup>a</sup> $m(\text{Et}_3\text{NHCl-AlCl}_3) = 2.6579$  g; reaction time: 4 h; solvent: CHCl<sub>3</sub>

**Polymerization temperature:** In order to investigate the importance of polymerization temperature, the polymerizations were performed at various temperatures. The results are shown in Table-4. It can be seen that  $\alpha_H$  increased with increasing temperature. The higher polymerization temperature, the more the cyclization reaction, the higher the softening point. The softening point also had a relationship with the molecular weight of copolymer and the molecular weight of copolymer decreased with increasing temperature, so the softening point did not always increase with increasing temperature. When polymerization temperature was -5 °C, it was found that the yield was 65.6 %.

In order to obtain a lighter colour and higher yield, it is preferable to operate at -5 °C. When polymerization temperature was -5 °C, a maximum softening point (95 °C) was achieved.

TABLE-4  
POLYMERIZATION OF C<sub>5</sub> REFINERY STREAM AND  
STYRENE AT VARIOUS TEMPERATURES<sup>c</sup>

Run	Temp. (°C)	Yield (%)	Softening point (°C)	Gardner colour	$\alpha_H$
1	55	61.6	84	3	0.7551
2	45	60.5	86	3	0.7341
3	35	59.6	93	3	0.7083
4	25	56.8	85	3	0.6763
5	15	38.3	80	3	0.6625
6	5	39.5	83	2	0.6572
7	-5	65.6	95	1	0.6513
8	-15	64.7	90	1	0.6290

<sup>c</sup> $w_{\text{styrene}} = 20\%$ ;  $m(\text{Et}_3\text{NHCl-AlCl}_3) = 2.6579\text{g}$ ;  $X(\text{AlCl}_3) = 0.69$ ; reaction time: 4 h; solvent:  $\text{CHCl}_3$

**Comparison among the properties of resins produced in different conditions:** The comparison among the resins produced in different conditions is listed in Table-5. The colour of resin produced with  $\text{Et}_3\text{NHCl-AlCl}_3$  as catalyst was greatly improved compared with  $\text{AlCl}_3$ . The use of styrene further improved the colour of resin. When the  $w_{\text{styrene}}$  was 20 %, the colour of copolymer was Gardner1 and the softening point of copolymer was a bit lower than with C<sub>5</sub> refinery stream's.

TABLE-5  
COMPARISON AMONG THE RESINS PRODUCED  
IN DIFFERENT CONDITIONS<sup>d</sup>

Run	Catalyst	Monomer	Yield (%)	Gardner colour	Softening point (°C)
1	$\text{AlCl}_3$	C <sub>5</sub> refinery stream	58.6	6	110
2	$\text{Et}_3\text{NHCl-AlCl}_3$	C <sub>5</sub> refinery stream	58.7	3	105
3	$\text{Et}_3\text{NHCl-AlCl}_3$	Styrene/C <sub>5</sub> refinery stream	65.6	1	95

<sup>d</sup>Solvent:  $\text{CHCl}_3$ ;  $X(\text{AlCl}_3) = 0.69$ ; reaction time: 4 h

## Conclusion

$\text{Et}_3\text{NHCl-AlCl}_3$  is an excellent catalyst for the cationic polymerization of styrene and C<sub>5</sub> refinery stream. The optimum reaction conditions for this reaction are as follows:  $w_{\text{styrene}} = 20\%$ ; solvent:  $\text{CHCl}_3$ ;  $m(\text{Et}_3\text{NHCl-AlCl}_3) = 2.6579\text{g}$ ;  $X(\text{AlCl}_3) = 0.69$ ;  $T = -5\text{ }^\circ\text{C}$ ; reaction time: 4 h. The softening point of the resin was 95 °C and the colour is Gardner1. The yield is 65.6 %; The use of  $\text{Et}_3\text{NHCl-AlCl}_3$  catalyst greatly improved the colour of resin and promises to afford easy catalyst recovery by simple phase separation. This process can be less corrosive, easier to handle and minimizing industrial waste water production; The use of styrene further improved the colour of resin.

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