

Use of a Supported Aluminium Chloride Catalyst for the Production of Hydrocarbon Resins¹

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Abstract:

Immobilised aluminium chloride containing both strong Lewis and Brønsted acid sites is shown to be an active catalyst for the cationic polymerisation of C5 aliphatic refinery feed-streams. Particular attention is given to the improvement in the yield, the properties of resin obtained and the ability to control resin properties by changes in the precise nature of the catalyst. The use of this solid acid has resulted in a reduction in the unwanted and hazardous waste that is produced during conventional homogeneous processes. The stability of the active species on the support in a typical batch polymerisation reaction process has been determined, and particularly low leaching levels have been found.

Introduction

Hydrocarbon resins are low-molecular weight, thermo-plastic materials that can be produced via the cationic polymerisation 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. Manufacture is highly dependent on the nature of the feedstock, the type of initiator, and the conditions of the polymerisation process itself. Generally speaking, the purer the feed, the easier it is to polymerise; for example, pure or concentrated piperylene is easier to polymerise than a C5 refinery stream. Pure monomers are, however, more expensive to produce than the refinery streams which are often by-products of large volume refinery processes. We have studied the polymerisation of C5 refinery feedstreams that are known to be difficult to polymerise. Such feedstreams contain polymerisable monomers such as cyclopentene, 1,3-pentadiene, and 2-methyl-2-butene. At present, polymerisation of such feedstreams is carried out using standard Lewis acids such as aluminium trichloride, alkyl aluminium halides, boron trifluoride, or complexes of boron trifluoride. The use of homogeneous catalysts poses many problems; their corrosive nature makes them difficult to handle, there is often the need for large amounts of catalyst in some reactions, they are difficult to separate from the organic products, and as a consequence of aqueous extraction procedures their disposal results in large quantities of toxic

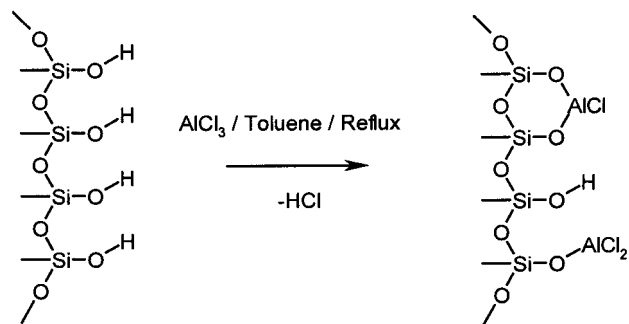


Figure 1. Preparation of supported aluminium chloride.

and corrosive waste. In 1995 Clark et al.² reported “an active heterogeneous form of aluminium chloride” (Figure 1).

Aluminium chloride is contacted with K100 silica in toluene at reflux temperatures for 2 h; at this temperature the aluminium chloride readily reacts with surface hydroxyl groups to create highly acidic species chemically bonded to the support. Drying the slurry under vacuum produces a yellow-coloured free-flowing powder. The use of this supported catalyst promises to afford easy catalyst recovery by filtration while being less corrosive, easier to handle, and minimising hazardous waste. This catalyst has been characterised previously in our laboratory by various methods;³ spectroscopic titrations with pyridine have shown the presence of both Lewis and Brønsted acid sites while information from MAS MNR experiments has led us to conclude that the principle active species is the Si–O–AlCl₂ moiety. Other workers have independently reported forms of supported aluminium chloride although their activities may not match the one described above.^{4,5}

Results and Discussion

Polymerisation reactions were carried out by the incremental addition of catalyst and feed to a continuously stirred batch reactor. The reaction proceeds under its own exotherm from room temperature to typically 40 °C; this temperature is sustained throughout the course of the 90 min reaction. In a normal homogeneous reaction the reaction is then quenched. Deactivation in a homogeneous system is achieved by adding a nucleophilic quenching agent to the reaction mixture to convert the residual Friedel–Crafts acids to

(1) Clark, J. H.; Lewtas, K.; Shorrock, J. K.; Garcia, L.; Wilson, K.; Chisem, J.; World patent application PCT/EP00/07083, 2000.

(2) Clark J. H.; Martin K.; Teasdale A. J.; Barlow S. J. *J. Chem. Soc., Chem. Commun.* **1995**, 2037.

(3) Price, P. Aromatic Alkylations Catalysed by Aluminium Chloride-Modified Mesoporous Silica. D. Phil Thesis, University of York, 1999.

(4) Drago, R. S.; Petrosius, S. C.; Chronister, C. W. *Inorg. Chem.* **1994**, *33*, 367.

(5) Schmidt, R. J.; Stine, L. O. U.S. Patent 4,783,575, Nov. 8, 1988.

Table 1. Comparison of Resin Properties Prepared with AlCl_3 and $\text{AlCl}_3/\text{SiO}_2$

	AlCl_3	$\text{AlCl}_3/\text{SiO}_2$	$\text{AlCl}_3/\text{SiO}_2$	AlCl_3	$\text{AlCl}_3/\text{SiO}_2$	silica
pretreatment	none	none	$\text{AlCl}_3/\text{SiO}_2$	water/ alumina	water/ alumina	none
yield	34	9	16	34	19	0
M_n	1160		1070	1310	1050	—
M_w	1790		1880	2760	1570	—
M_z	2820		3350	3770	2360	—
M_w/M_n	1.54		1.76	1.73	1.69	—
softening point/ $^{\circ}\text{C}$	88	54	60	87	56	—
Gardner color	3.3	3.5	3.0	2.3	2.3	—

conveniently disposable species. The organic and aqueous phases are then separated by simple phase separation. In the heterogeneous system considered here, removal of the catalyst from the polymerisate was achieved by simple filtration. In both cases the polymerisate was steam-stripped to remove the solvent and low-molecular weight oligomers. The resultant resin was characterised by yield, GPC, and softening point.

Although yield is an important factor in resin synthesis, molecular weight and softening point also have important significance when considering the compatibility of the resin in its final end application. Changes to the main parameters of this cationic polymerisation reaction and hence effects on the yields and polymer properties have been studied, and optimisation of reaction conditions for the production of a commercially viable resin using a solid acid catalyst is herein discussed.

Feed Pretreatment. Preliminary investigations for the replacement of aluminium chloride with our solid acid catalyst gave promising results; however, under initial experimental conditions the silica-supported aluminium chloride was considerably less active than homogeneous AlCl_3 for polymerisation (Table 1). It was thought that the catalyst was being poisoned by the irreversible adsorption onto the active sites of small amounts of impurities such as peroxide, carbonyl, and sulphur species that are inevitably contained within refinery feed-streams and the levels of which can vary according to the raw distillate material, the cracking process, and transport and storage methods. Adverse effects from these poisons can be manifested in reduced activity and lower yields. The yield of the heterogeneous polymerisation reaction has been much improved by the introduction of a feed pretreatment stage that acts to clean the feed prior to polymerisation. Initially, stirring immobilised aluminium chloride in the feed under conditions not conducive to bulk polymerisation (for example, short contact times and low catalyst amounts) resulted in a significant increase in yield in the subsequent polymerisation. The supported material, with poisons absorbed, was removed by filtration from the feed prior to reaction. The feed was analysed, prior to and after the pretreatment, for carbonyl, sulphur and peroxide species as well as by GC for analysis of monomer concentrations. It was found that the levels of carbonyl, sulphur, and peroxide species had been reduced by 207, 12, and 58 ppm, respectively. Since no change was

seen to the concentration of monomers, we can confirm that the increase in yield seen is due to removal of the poisons.

The time required for the pretreatment to be effective was also investigated; a pretreatment time of 7 min was as successful as 90 min. Since basic species will rapidly combine with acid sites, these results corroborate our feed-cleaning theory. Subsequent pretreatment investigations established that washing the feed with water prior to contact with basic activated alumina provided a particularly effective means of reducing poison levels (reductions of 309, 12, and 54 ppm for carbonyl, sulphur, and peroxide respectively) with the result that the resin yield is significantly increased compared to that of a nontreated reaction, whilst polymer properties (molecular weight distribution and softening point) are maintained. An identical water/alumina pretreatment was carried out on the feed prior to a polymerisation reaction with homogeneous aluminium chloride. No increase in yield was seen, nor was any change in molecular weight determined. We can conclude that the supported catalyst is more sensitive to poison levels in the feed than its homogeneous counterpart, which is typical of a heterogeneous catalyst system. Feed cleaning prior to the polymerisation process has the added benefit of producing a feed of consistent quality from reaction to reaction, and we can now exercise much tighter control over the polymerisation process and hence of the resin obtained (adsorption of poisons is an exothermic process, temperature is a most valuable parameter for molecular mass control: molecular mass increases with decreasing reaction temperature).

As mentioned, it is not only yield that is important in the commercial production of hydrocarbon resins, molecular weight distribution is also important. Since the polymer properties obtained with the supported catalyst are consistent with those of the homogeneous catalyst, the difference in yield, although disappointing, has not proven to be a setback since unreacted feed can simply be recycled.

The ratio of the weight-average to the number-average (M_w/M_n), otherwise known as the polydispersity, is another factor to be considered in the synthesis of hydrocarbon resins. Narrow polydispersity is important to ensure compatibility of the resin with polymers in end use applications. We have achieved here with the supported catalyst similarly narrow polydispersities compared to the homogeneous catalyst. The softening points for the resins produced via the solid acid-catalyzed route are, however, consistently lower than those obtained via the standard homogeneous AlCl_3 route. This shows that this property is not simply related to molecular weight alone. Aliphatic resins are not simply straight-chain polymers but also contain cyclic structures formed by internal cationic cyclisations.⁶ Such structures can increase the softening point. Work is continuing to determine if this is the cause of the difference in softening points.

Another important characteristic of hydrocarbon resins is colour. Colours of commercially available resins range from water-white, through light yellow, yellow, yellow-brown, to dark brown. Colour of resins synthesised here have been

(6) Mildenberg, R.; Zander, M.; Collin, G. *Hydrocarbon Resins*; VCH Verlagsgesellschaft mbH: Weinheim, 1997.

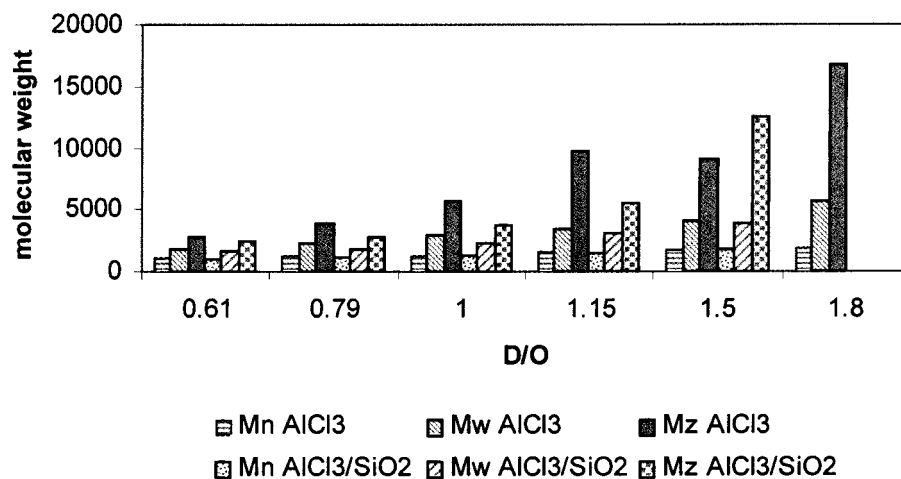


Figure 2. Molecular weight distribution for supported aluminium chloride and homogeneous aluminium chloride at different di-olefin to mono-olefin ratios.

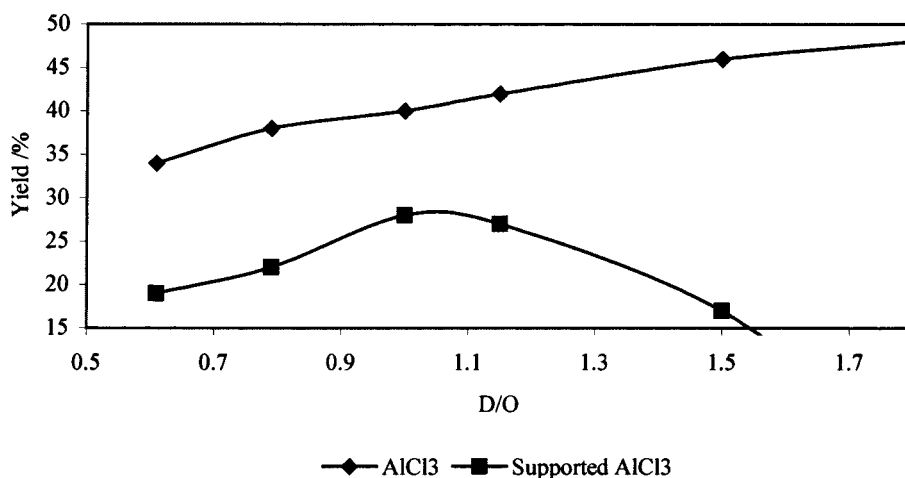


Figure 3. Effect of changing the D/O ratio of the feed on the yield of the two catalysts.

determined by the Gardner standard method. Resins produced via the supported catalyst system have the same colour quality as the homogeneous catalyst. Pretreatment especially with water/alumina also seems to improve the colour.

Changes in Feed Composition. We have seen that the molecular weight distribution of a resin must be tightly specified for it to be compatible with an end use application. Control of molecular weight is thus of fundamental importance; in a homogeneous system this can be achieved by careful modification of the feed with controlled amounts of chain-transfer agents usually mono-olefins as opposed to di-olefins (in this case 2-methyl-but-2-ene and derivatives of). Experiments were performed with varying amounts of chain-transfer agents (the x -axis represents the ratio of di-olefins to mono-olefins, D/O,) (Figure 2).

M_n and M_w values obtained with the supported catalyst are, within error, the same as for the homogeneous catalyst. Generally however, much lower M_z values are noted for the heterogeneous catalyst, this maybe due to the limitations of the pore cavity physically restricting the length of the polymer chain. Low M_z values are of particular interest and importance since they translate to increased compatibility of the resin with other components in an adhesive formulation. For example, although a 48% yield can be achieved

with the homogeneous catalyst at a di-olefin-to-olefin ratio (D/O) of 1.8 the M_z value, 16800, is too high for use in an adhesive formulation (Figure 3).

Despite these promising results we can see resin yields with the supported system drop rapidly to effectively zero (yield too low to measure) as the D/O ratio is increased (Figure 3). As a consequence this method of controlling the molecular weight via feed modification cannot really be applied to the system especially if a commercial application is in mind. We have found, however, a method exclusive to the heterogeneous system that does allow such control and that is modification of the support material (discussed later).

The softening points of resins obtained at these various feed ratios were also determined; a large range can be achieved with supported aluminium chloride from medium high (70–80 °C) to low (50–70 °C). High softening point resins have yet to be made. It is thought that the physical dimensions of the silica-pore size restrict the reactions leading to cyclisation. Work is in progress to find the appropriate conditions, possibly by modification of the porous structure, to produce a higher softening point resin.

Modification of the Support Material. We have found that the temperature to which the silica is exposed prior to formation of the catalyst has important consequences for both

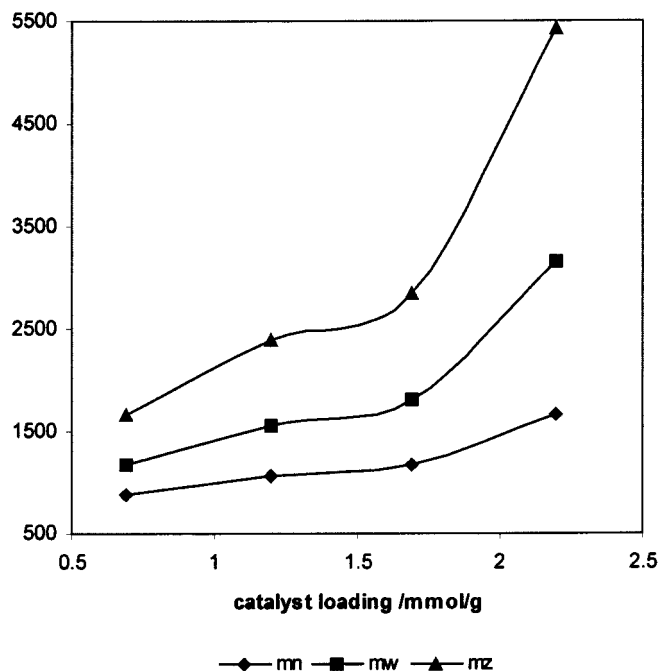
Table 2. Effect of the Modification of the Silica Surface on Resin Properties

catalyst	AlCl ₃ /SiO ₂			silica			AlCl ₃	
silica	300	600	300	300	300	300	—	300
temperature/°C								
loading/mmolg ⁻¹	1.69	1.69	0.69	1.2	2.2	0	—	0
yield	22	32	10	19	22	0	38	31
<i>M_n</i>	1170	1430	890	1060	1670	—	1370	1270
<i>M_w</i>	1810	2650	1180	1550	3150	—	2290	2250
<i>M_z</i>	2840	6000	1670	2400	5430	—	3880	3500

the yield and the molecular weight of the resin obtained. A reaction carried out with aluminium chloride supported on silica calcined at 600 °C showed increased activity when compared with the same catalyst made with silica calcined at 300 °C (Table 2). The molecular weight of the resin is also increased with silica calcination at the higher temperature. The surface species on unmodified amorphous silica are highly temperature-dependent; heating from ambient to 150 °C removes physisorbed water from the silica surface, while further heating steadily converts surface hydroxyl groups into siloxane bridges and remaining hydroxyl groups become more and more isolated.⁷ Calcination temperatures of around 600 °C irreversibly modify the silica surface so that the concentration of hydroxyl groups is severely reduced and any remaining are completely isolated from each other on the surface. It is apparent that exposure to hydroxyl species greatly affects the polymerisation reaction. With this in mind, catalysts were synthesised with different aluminium chloride loadings, the lower the loading, the more the exposure to surface hydroxyl groups (Table 2).

By adjustment of the amount of catalyst used an equal number of active sites were available in each reaction. No difference in activity is expected; however, we find a drop in activity as the catalyst loading is lowered. It would seem that close proximity of a hydroxyl group to an active site results in decreased activity. Investigations by Drago and co-workers have shown that the amount of silanol groups available for reaction with AlCl₃ is critical to the acidity of the resulting catalyst.^{8,9} Figure 4 shows the trend in molecular weight against catalyst loading. Between loadings of 0.69–1.69 mmol g⁻¹ an almost linear increase in molecular weight is seen. Above this a sharp increase in the molecular weight is seen, suggesting a homogeneous contribution to the reaction. Work by Price³ has shown that a loading of 2.2 mmol g⁻¹ is above the optimum for the support and that at this loading there was an increased likelihood of free AlCl₃ on the support surface. Indeed we do see a homogeneous contribution to the reaction; as mentioned high *M_z* values are a feature of a homogeneous catalyst system.

We have seen lower-molecular weight polymers produced when using catalysts of lower loadings or made from silica at lower calcination temperatures. We suggest that the molecular weight of the polymer is dependent on the concentration of silanol groups to which it is exposed. When

**Figure 4.** Molecular weight values with different catalyst loadings.

unmodified silica is added to a homogeneous reaction, the resin obtained also has lower-molecular weight values than expected. The silica surface, or hydroxyl groups, may effectively be functioning as a chain-transfer agent. The yield is also decreased relative to the usual reaction; that is to say that the rate of chain termination relative to that of propagation is much faster. It is also possible that the rate and degree of polymerisation is influenced by different relative concentrations of the active sites such as $-O_2AlCl$ groups. Whatever the reason, it seems that by careful choice and modification of the support we have here in the supported catalyst system a handle by which we can tune the molecular weight to provide a variety of commercially useful resins.

Catalyst Stability. For the advantages of a solid acid catalyst to be realised we must have a system that is truly heterogeneous; that is to say, the catalyst must be stable under the reaction conditions, and no leaching of acid moieties into the resin should be observed. Prevention of chloride leaching into the reaction system has particular benefits, especially if the raffinate is subsequently used as a fuel component where there is a need for lower chlorine levels or if the resin is further treated in a technique such as hydrogenation where chlorine can damage the catalyst or the hydrogenation unit.

(7) Vansant, E. F.; Van Der Voort, P.; Vrancken, K. C. *Studies in Surface Science and Catalysis*; Elsevier Science B. V.: Amsterdam, 1995.

(8) Drago, R. S. *J. Am. Chem. Soc.* **1988**, *110*, 3311.

(9) Drago, R. S. *Inorg. Chem.* **1990**, *29*, 1186.

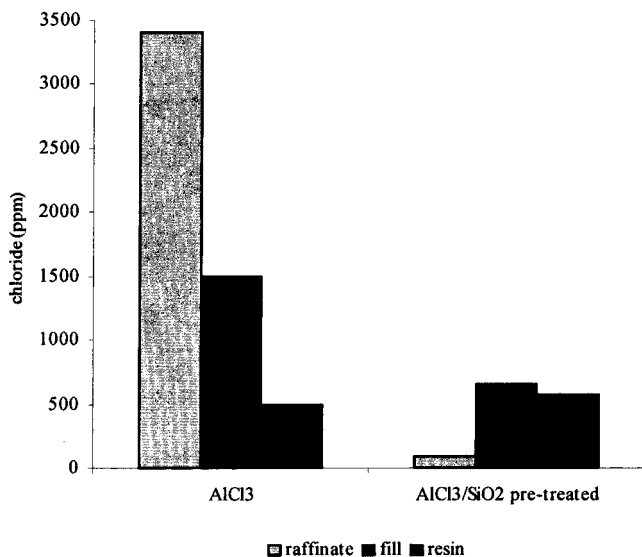


Figure 5. Comparison between the chloride levels in the raffinate, fill, and resin produced by AlCl₃ and AlCl₃/SiO₂.

Feed polymerisations with AlCl₃/SiO₂ (pretreated with water/alumina) resulted in much lower chloride levels in both the fill and raffinate, while chloride values of similar magnitude were obtained in resins when compared to a homogeneous reaction (Figure 5). Only low levels of aluminium were found in the resin, fill, and raffinate (42, 0.07, 0.05 wt·ppm respectively). We believe that the Si–O–Al–Cl₂ species is stable under the reaction conditions, and as such, leaching of acid moieties is particularly low.

Conclusions

The use of a solid acid catalyst as a replacement for conventional homogeneous AlCl₃ in the cationic polymerisation of a C5 feed-stream was investigated. The following conclusions as to its suitability have been made:

1. The activity of supported aluminium chloride towards polymerisation is lower than the present homogeneous system.

2. M_n and M_w values of resins produced via the two systems are favourably comparable. The solid acid catalyst produces resins with a lower, more desirable M_z value.

3. Washing the feed with water and then drying over alumina increases the resin yield using the supported catalyst and also acts to improve the colour.

4. The softening point of resins produced with the supported catalyst is lower than with AlCl₃. Modification of the silica surface is currently under way to improve the softening points.

5. Polymer properties of resins produced with the supported catalyst can be controlled by the modification of the silica support.

6. Particularly low chloride and aluminium levels have been found in the fill, raffinate, and resin produced with this

solid acid. This, as well as having important financial implication, indicates particularly low leaching levels of the acid moieties.

Experimental Section

General Procedures. GPC analysis was carried out at Exxon Laboratories. Yield was determined by expressing the mass of the resin produced after stripping as a percentage of the total mass of feed used (including solvent). Resin colour was determined via the Gardner method: a 50% solution of resin in toluene is compared with a set of standard colour disks. Ring and ball method ASTM D 3461 was used for determination of the softening point of resins. Chlorine and aluminium content were determined by ICP-AES.

Typical Preparation of Supported Aluminium Chloride. Aluminium trichloride, 2.25 g (16.9 mmol), was added to 70 mL of sodium-dried toluene. The support material, 10 g (K100 silica), was dried prior to contacting the aluminium trichloride for 24 h at 300 °C. The dried support material was added to the aluminium trichloride solution and the resulting slurry stirred at reflux for 2 h. The solvent was removed under vacuum at room temperature to obtain a flowable powder. Prior to use, the catalyst was stored and handled in an inert atmosphere.

Typical Procedure for a Feed Polymerisation Reaction Using Supported Aluminium Chloride. A 2 L elongated flange flask with a bottom outlet tap was equipped with an overhead stirrer, reflux condenser, gas inlet, thermocouple, and a dropping funnel. The flask was charged with a slurry of 2.5 g of supported catalyst in 15 mL of anhydrous toluene. C5 aliphatic feed (600 g) and 16 g of supported aluminium chloride were added in increments over 45 min to the nitrogen-purged flask via the dropping addition funnel and self-adapted glass tube, respectively. In some cases the feed was pretreated by washing with water, 1 part feed to 5 parts water, and then dried over basic activated alumina. The reaction solution was stirred at room temperature for a total reaction time of 90 min. The resulting resin solution was separated from the catalyst by filtration at room temperature. The volatile components and solvent were removed by steam-stripping the polymerisate at 250 °C to remove unreacted material and low-molecular weight oligomers.

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