

Chemically modified mesoporous solids and their use in the polymerisation of hydrocarbon monomers

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The controlled reaction of Lewis acids with mesoporous silica can be used to prepare solid cationic initiators useful for the polymerisation of hydrocarbons. These materials not only offer the advantage of enabling simpler processes and reduced waste but also show interesting and often dramatic differences from the behaviour of conventional homogenous cationic initiators due to solid surface and pore effects.

Introduction

Petroleum resins are produced *via* the cationic polymerisation of monomer feedstreams which can be pure monomers or refinery streams containing mixtures of various unsaturated as well as saturated compounds. Petroleum resins are used in adhesives, rubbers, hot-melt coatings, printing inks, paint, flooring and other applications. The polymerisation reactions are typically carried out using Lewis acids, notably aluminium trichloride, alkylaluminium halides and boron trifluoride. These homogenous catalysts suffer from the disadvantages of difficult handling (including health and safety issues) and the need to use a quench step at the end of the process to remove the catalyst. This quench not only destroys the catalyst but also generates hazardous waste which in these environmentally conscious days is undesirable and can be expensive to deal with. The potential for replacing these soluble Lewis acids with solid acids is considerable, since the latter are normally safer and easier to handle, and separable by filtration or other non-destructive and non-waste-generating means.

The first patents in this area were published in the late 1990s.¹ We have recently reported results from some of our studies on the use of two solid acids developed in York, supported aluminium chloride² and supported boron trifluoride complex,³ in the polymerisation of some common refinery mixed feeds.⁴ We now report results from the use of these solid acids to initiate the polymerisation of common refinery monomers and mixtures of monomers. Our results reveal additional benefits from using the solid initiation systems, notably in the quite different properties of the materials produced. They also show some remarkable and unpredictable effects of one substrate on another.

Results and discussion

Polymerisation of aliphatic monomers using supported aluminium chloride

(i) **Mechanism of initiation of polymerisation *via* a supported aluminium chloride reagent.** Supported aluminium chloride is known to possess both Brønsted and Lewis acid sites.² To investigate the mode of initiation of the cationic polymerisation of hydrocarbons, experiments were performed whereby the proton blocker 2,6-di-*tert*-butyl-4-methylpyridine (DBMP) was added to supported aluminium chloride in toluene in variable amounts prior to addition of 1,3-pentadiene (PD) (Fig. 1). The resulting plot shows three sections, in the first of these an

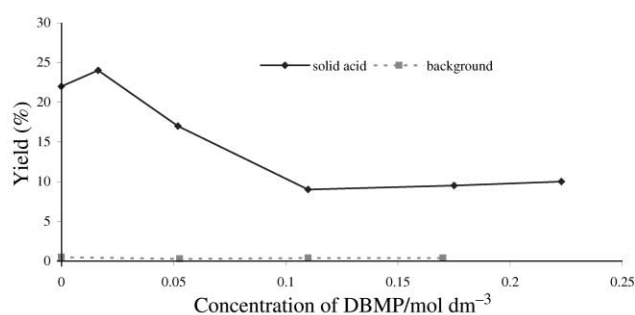


Fig. 1 Effect of adding DBMP to the polymerisation of PD.

increase in yield is observed which is explained by the trapping of protonic impurities *e.g.* water that would otherwise adversely affect the polymerisation process by poisoning of the catalytically active sites. At higher concentrations of DBMP, there is a linear decrease in polymer yield consistent with proton trapping removing one initiation source. At a DBMP concentration of 1.1 mmol g⁻¹ silica this linear dependence ceases and additional DBMP has no effect. At this point the product yield is about 1/3 of that obtained in the absence of the proton trap. These results are consistent with a dual mechanism that allows both Brønsted and Lewis acid sites to initiate the reaction and with a solid acid that has Brønsted and Lewis acid sites in a 2 : 1 ratio. The dual mechanism is also witnessed by the molecular weight analysis under different initiation mechanisms. In the absence of DBMP, two broad bands are seen using gel permeation chromatography, GPC (M_w ca. 3.2K and 3.9K) and can be assigned to initiation by Brønsted and Lewis acid sites respectively. As the amount of DBMP in the reaction increases the intensity of the two bands relative to each other changes, the band at higher molecular weight becoming more intense as the degree of catalysis by Lewis sites predominates. Indeed, at high DBMP concentrations (0.11 and 0.175 mol dm⁻³) the molecular weight distributions of the polymers show very similar profiles since at both these concentrations the polymer is formed solely *via* direct initiation due to the Lewis acid sites.

(ii) **Evidence for heterogeneous initiation.** It is clear that protic initiation is the major mechanism under which supported aluminium chloride operates. Protons in this system can arise from (i) surface OH groups, (ii) water, (iii) HCl (formed during the preparation of the catalyst). Polarisation of a water molecule by an adjacent aluminium site may sufficiently enhance its acidity for it to be effective for polymerisation

(water is the predominant co-catalyst in homogeneous systems). If initiation were by water co-catalysis it would be expected that a reaction quenched by DBMP could be reactivated by the addition of water as long as it was added in greater quantity than that of the DBMP used and there was sufficient Lewis acid remaining. However, no increase in yield was found suggesting that water is not a co-catalyst in this system. As for HCl, addition of pure HCl to a monomer system gives little polymer (<5%). Furthermore, after DBMP addition to a supported aluminium chloride initiated reaction, NMR analysis shows only DBMP and no DBMPH⁺ in solution consistent with the protic source being on the solid surface. Diffuse reflectance FTIR confirms the presence of DBMPH⁺ on the silica surface.

Interestingly, addition of gaseous HCl to a normal supported aluminium chloride–PD–toluene polymerisation system increases the yield of polymer from *ca.* 22 to *ca.* 61%. This is presumably due to polarisation of the HCl by Al centres giving enhanced Brønsted activity.

The OH groups on silica are not themselves acidic enough to promote the polymerisation reaction; addition of silica to a monomer system gives little polymer (<5%). It is suggested that OH groups adjacent to an aluminium chloride species on the silica surface are polarised and do have sufficient acidity to initiate polymerisation. The effect of OH group concentration on the surface of the supported reagent was investigated (Fig. 2). The concentration of available protons increases with

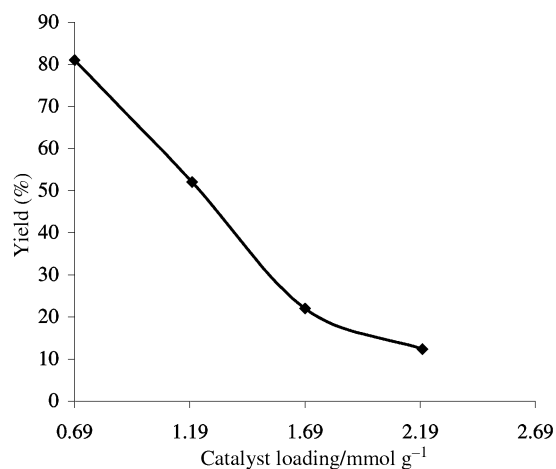


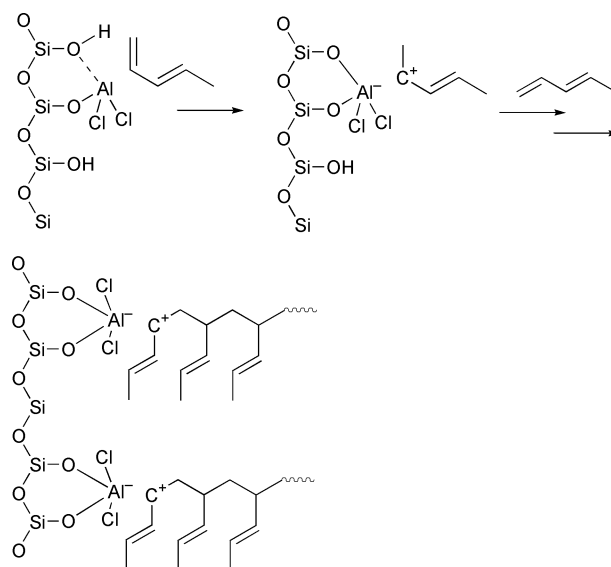
Fig. 2 Effect of catalyst loading on polymer yield.

decreasing loading of aluminium centres since more OH groups are available for polarisation. As the availability of the co-catalytic hydroxyl groups increases (decreasing loading) a corresponding increase in yield is obtained. A decrease in yield was also observed upon increased calcination of the support material; OH group concentration decreases as the temperature at which the silica is precalcined prior to catalyst synthesis is increased. It is proposed both that surface hydroxyl groups adjacent to Lewis acid centres become polarised inducing sufficient acidity to promote polymerisation and that this is the predominant form of initiation. GPC results also indicated a shift to lower molecular weights as the Brønsted acid character of the reagent increased.

(iii) **Nature of the aliphatic polymer: cross-linking.** The cationic polymerisation of PD usually produces both soluble and insoluble cross-linked polymer.^{5,6} Cross-linking is considered to be a major side-reaction wherein the propagating active species attacks a double bond of a polypentadiene (PPD) chain, the resulting cation then undergoes subsequent attack by a PD molecule to form an insoluble gel. Given that the reduction or elimination of gel formation has been the focus of many,

sometimes quite elaborate, studies⁷ it was rather surprising to discover that the formation of cross-linked products was not observed under any of the reaction conditions (different temperatures, solvents, catalyst amount *etc.*) when polymerising pentadiene with supported aluminium chloride. Table 1 compares the polymerisation when using homogeneous and heterogeneous AlCl₃ for the polymerisation of PD in toluene.

For AlCl₃ the amount of insoluble material increases with the monomer concentration, and moreover, since all yields are around 95%, with the amount of polymer in the reaction solution. The extent of the cross-linking reaction is expected to be dependent on the polymer concentration in this way since there is greater opportunity for an active centre to attack a polymer double bond if the polymer concentration is higher. No cross-linked polymer is found even at yields of 76% when using the supported catalyst. This may perhaps be a reflection on the fact that lower yields obtained with the supported catalyst reduces the polymer concentration in the reaction system compared to that for the homogeneous catalyst. Reactions carried out with the supported catalyst in the presence of added polymer however, also showed no sign of cross-linked material. It is evident that the intermolecular reaction of cross-linking does not happen with the supported catalyst. It is proposed that the active cation is held close to the support by an ionic interaction and as such it is highly improbable that the cation is able to come into contact with another polymer chain and so reactions leading to cross-linked products are eliminated (Scheme 1).



Scheme 1 Initiation and propagation of monomers held *via* ionic interactions to the support.

(iv) **Nature of the aliphatic polymer: cyclisation.** The degree of cyclisation in a hydrocarbon resin is known to affect the properties of the polymer with a high degree generally being preferred for example, in adhesive formulations. Mixed petroleum feeds may give relatively low degrees of cyclisation when using supported catalysts⁴ so in order to study this important phenomenon further, we have looked at the effects of some variables on the degree of cyclisation in solid acid-initiated single monomer polymerisations.

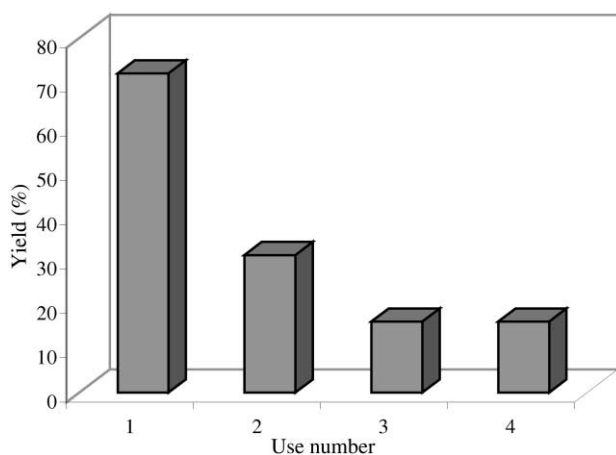
We firstly looked at the possible effects of different initiation sites. This was achieved through the use of variable amounts of the proton blocker DBMP. The degree of cyclisation of 1,3-PD using supported aluminium chloride (measured as the loss of unsaturation in the product by ¹H NMR) is essentially independent of the concentration of DBMP suggesting that the mechanism leading to cyclisation does not involve an intermediate protic species. This is consistent with results reported

Table 1 Degree of cross-linking product obtained when using homogeneous and supported aluminium chloride

Catalyst	Amount of PD/ml	Soluble polymer (%)	Cross-linked product (%)	Total (%)
AlCl ₃ /SiO ₂	1	76	0	76
AlCl ₃ /SiO ₂	3	32	0	32
AlCl ₃ /SiO ₂	7	22	0	22
AlCl ₃ /SiO ₂	10	8	0	8
AlCl ₃	1	95	2	97
AlCl ₃	3	64	31	95
AlCl ₃	7	33	62	95
AlCl ₃	10	13	80	93

elsewhere for the FeCl₃-initiated polymerisation of 1,3-PD.⁶ Since a protonic mechanism has been eliminated it is proposed that the active species for cyclisation is the same as that which causes propagation. This is further supported by observation that during the short time period of polymerisation, yield and degree of cyclisation increase together. Once the polymerisation is complete, there is no further change in the degree of cyclisation with time. Santarella *et al.* have proposed two mechanisms whereby cyclic species could form.⁵ The first of these is intramolecular where the cation from the active propagating species attacks a double bond in the same polymer. The second is bimolecular involving attack on a second polymer chain. We believe that our results are more consistent with a unimolecular process especially since the cation is bound by an ionic interaction to the support and as such is not available to react with a double bond on another polymer chain, just like cross-linking. It is suggested that the cation can only induce cyclisation in the adjacent double bond, which can then cause further cyclisations in a step wise ladder type process.

(v) Pore blocking and reuse of the solid initiator. At high monomer concentrations, polymer yields are low. Since the solid initiators are porous, it seems possible that pore blockage may be a significant factor (higher concentrations of solvent would allow the polymer to be 'flushed' from the pores). This is confirmed by analysis of supported aluminium chloride after use in, for example, the polymerisation of 1,3-PD. The surface area of the solid is reduced from 323 to only 25 m² g⁻¹ with a corresponding reduction in pore volume from 0.89 to 0.11 cm³ g⁻¹. Additionally, the pore size distribution shows a shift in the average pore diameter from 107 to 180 Å consistent with only the larger pores being available for absorption. The presence of a large quantity of adsorbed polymer is confirmed by thermal analysis which shows a major weight loss at *ca.* 300 °C (in addition to smaller lower temperature weight losses which can be attributed to traces of solvent and unreacted monomers). This will not only reduce the measured yield of product, it will also severely restrict reuse of the solid acid as shown in Fig. 3. We are currently working on ways of reducing product

**Fig. 3** Effect of catalyst reuse on yield.

retention by the solid acid as well as regenerating the source of protons to allow effective reuse.

Polymerisation of aromatic monomers using a supported BF₃ complex

(i) Homopolymerisation initiated by supported BF₃. The cationic polymerisation of two typical refinery aromatic monomers, indene and α -methylstyrene (α -MS) has been investigated using silica supported BF₃-ethanol complex. The reactions were performed under non-isothermal conditions; the reaction exotherm monitored and the kinetic data obtained compared with ¹H NMR data. The concentration of the monomers in the solvents (hexane, toluene or mixture hexane-toluene) was varied from 10 to 50 wt%.

Fig. 4 reports some typical kinetic data for the polymerisation

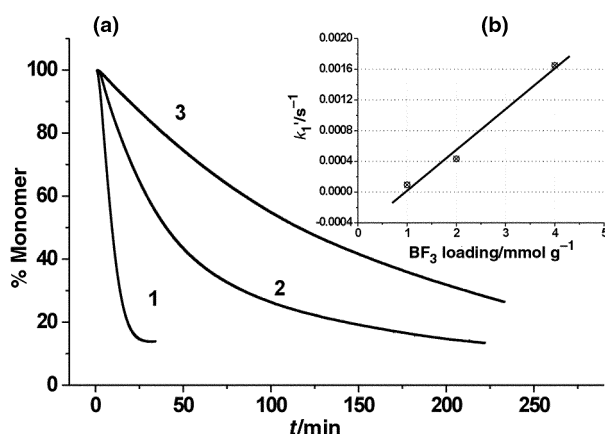


Fig. 4 Typical kinetic data for the polymerisation of α -MS in the presence of a supported BF₃ reagent. a = kinetic curves for different BF₃ loading: 1: 4 mmol g⁻¹; 2: 2 mmol g⁻¹; 3: 1 mmol g⁻¹. b = Dependence of first-order kinetic constant of the α -MS polymerisation *versus* BF₃ loading. *T*₀ = 293 K. The reaction mixture composition is: 30 ml α -MS; 60 ml heptane.

of α -MS in the presence of a supported BF₃ reagent at different loadings. From these curves it is noted that α -MS reacts quickly (reaction time is in the range of 10 minutes for 4 mmol g⁻¹ BF₃ loading), without an induction period. This is a first order reaction and as such the kinetic equation may be written as:

$$\frac{d[\text{Monomer}]}{dt} = -k_1'[\text{monomer}]$$

Fig. 4b shows that a linear dependence of the kinetic constant *k*₁' *versus* BF₃ loading exists; the line does not pass through the origin of the co-ordinates indicating that the catalyst is destroyed by poisons formed on the silica surface. The poison concentration is approximately 1.0 mmol per 1 g SiO₂.

In contrast to α -methylstyrene, the reaction of indene is slow, typically taking some 20 hours to reach 100% conversion

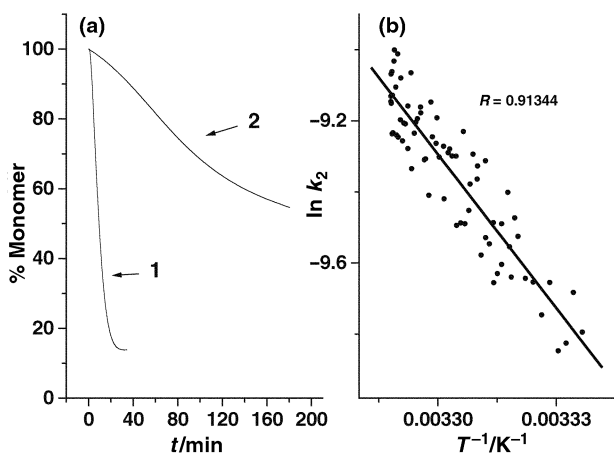


Fig. 5 Typical kinetic data for the polymerisation of indene in the presence of a supported BF_3 reagent in non-isothermal conditions. a = the original kinetic data of the α -methylstyrene (1) and indene (2) polymerisation, b = relationship of the logarithm of the second order constant of the indene polymerisation with inverse temperature. $T_0 = 293 \text{ K}$. The reaction mixture composition is: 20 ml of monomers; 20 ml toluene; 40 ml heptane. Loading BF_3 : 4 mmol g.

(Fig. 5a). Under non-isothermal conditions, the plot of kinetic data for the polymerisation of indene shows a long induction period (S-form). This may be explained by the peculiarity of the kinetic constants; it can be shown from Fig. 5b that indene polymerisation is a second order reaction. This is supported by the linear relationship of the logarithm of the second order constant ($\ln k_2$) with inverse temperature (Fig. 5b). k_2 could be calculated from experimental data by the equation:

$$k_2 = -\frac{1}{[\text{Indene}]^2} \frac{d[\text{Indene}]}{dt}$$

The activation energy of the heterogeneous indene polymerisation calculated from the Arrhenius equation for k_2 is 140 kJ mol^{-1} (E_a for the α -MS is 20 kJ mol^{-1}). A combination of both of these factors (high activation energy and second order kinetics) may result in the long induction period observed under non-isothermal conditions (due to a high activation energy) and the long reaction time (due to the second order reaction).

(ii) Co-polymerisation of monomers. It is of interest to consider what happens when the polymerisation of mixtures of monomers takes place. The polymerisation of an indene- α -MS mixture at various indene concentrations (100, 90, 75, 50 and 0%) was carried out. The results are shown in Fig. 6. The rate of polymerisation of the mixture is much higher than for indene alone; it is in fact very close to that for the polymerisation of α -MS. Some kinetic constants obtained from this data by non-linear fit are shown in Table 2.

GPC traces of the co-polymers obtained are shown in Fig. 7. The molecular weight of the co-polymers lies between that of indene and of α -MS and is closer to α -MS. It is of interest to note that molecular weight distribution does not change with monomer concentration and the addition of a small amount of α -MS (10%) dramatically changes the molecular weight distribution. So, the kinetic parameters associated with the properties of the catalyst (reaction time, molecular weight of the obtained polymers) drop sharply with increasing α -MS concentration. The kinetic parameters depend on the key parameters of the reaction (order of the reaction and activation energy) and are proportional to α -MS concentration.

The formation of a co-polymer is in good agreement with IR and TG-IR data (Fig. 8). The figure shows the IR spectrum of the polymer, obtained from the 50% indene and 50% α -MS

Table 2 Kinetic constants of the polymerisation of indene- α -MS mixtures

Concentration (%)		Order (n)	$E_a/\text{kJ mol}^{-1}$	Time/min
Indene	α -MS			
100	0	2.2 ± 0.2	139	≈ 1200
90	10	2.3 ± 0.2	137	60
75	25	1.9 ± 0.1	118	40
50	50	1.2 ± 0.1	82	15
0	100	1.0 ± 0.05	20	7

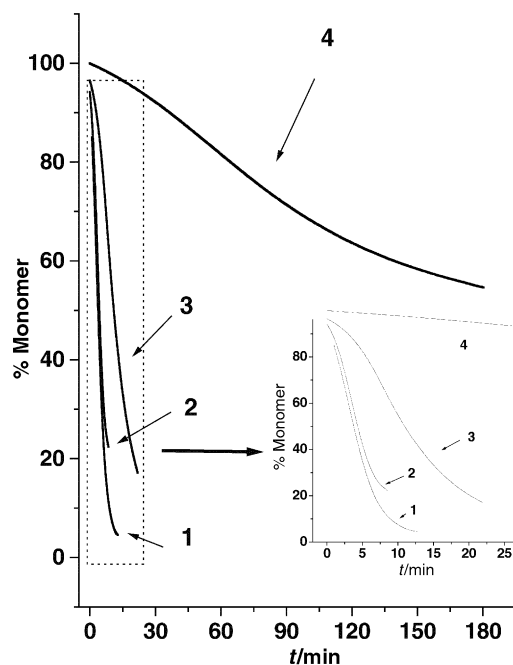


Fig. 6 Kinetic data of the polymerisation of indene and α -MS mixtures at various indene concentrations 1 = 50%, 2 = 75%, 3 = 90%, 4 = 100%. The reaction mixture composition is: 20 ml monomers; 20 ml toluene; 40 ml heptane. Loading BF_3 : 4 mmol g^{-1} .

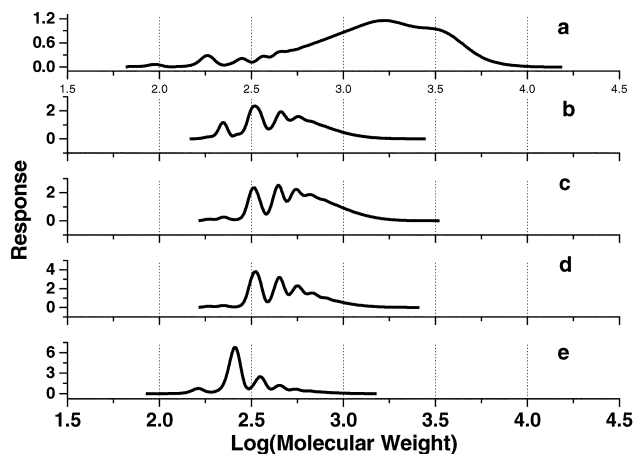


Fig. 7 GPC traces of the co-polymers obtained. a = indene; b = 90%; c = 50%; d = 30% indene; e = α -MS.

mixture. Spectrum "a" is that of the polymer film. Spectrum "b" is the gas-phase spectrum of the products of the polymer decomposition in a TG-IR experiment performed at $300 \text{ }^\circ\text{C}$. Spectrum "c" is the result of the summation of the indene and α -MS spectra found in the literature, with coefficients 0.665 and 0.335 respectively. The coefficient has been calculated by means of linear FIT. It does not change during the TG-IR experiment and completely agrees with the one obtained for the polymer film. In addition there is only one mass loss peak in the dTG spectrum.

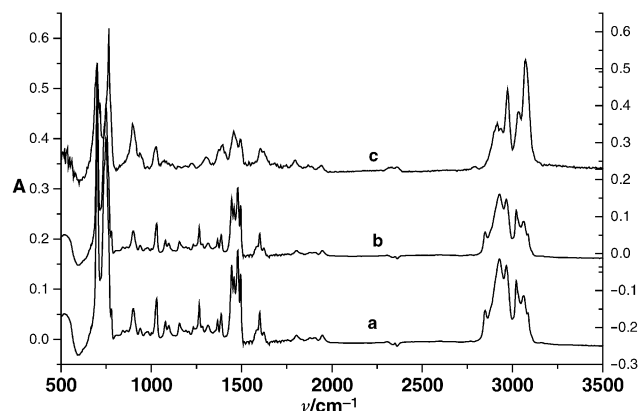


Fig. 8 The IR spectrum of the polymer obtained from 50% indene and 50% α -Ms mixture. a = the spectrum of the polymer film, b = the gas-phase spectrum of the products of the polymer decomposition in the TG-IR experiment, c = the theoretical spectrum of the mixture.

(iii) **Evidence for heterogeneous initiation.** A lot of experiments have been carried out in order to understand the mechanism of initiation in the presence of BF_3 supported on silica; these include influence of the solvent and products on the kinetic parameters of the reaction and the physical properties of the catalyst before and after polymerisation. The results of these experiments will be detailed in a further paper but suffice it to say that all the data obtained prove that initiation is truly heterogeneous, however, the main result of interest here is the reuse of the catalyst. Kinetic data of the first and second reaction (reuse) are shown (Fig. 9). It can be clearly seen that the catalyst shows excellent retention of activity on reuse.

Experimental

The monomers and solvents were commercial samples from Aldrich used without pretreatment. Results were reproducible even when using compounds reported as having purities as low as 90%. In a typical polymerisation the solid acid (1 g of either 1.69 mmol g^{-1} aluminium chloride supported on K100 silica² or 4 mmol g^{-1} boron trifluoride-ethanol complex supported on K100³) was added to the solvent (10 cm^3) under a nitrogen atmosphere and equipped with a magnetic stirrer. The monomer (typically 7 cm^3) was added *via* a syringe through a rubber septum. After reaction, the solid acid was removed by filtration. All products with the solid initiator are soluble and the product solutions were concentrated under vacuum at 60°C to constant

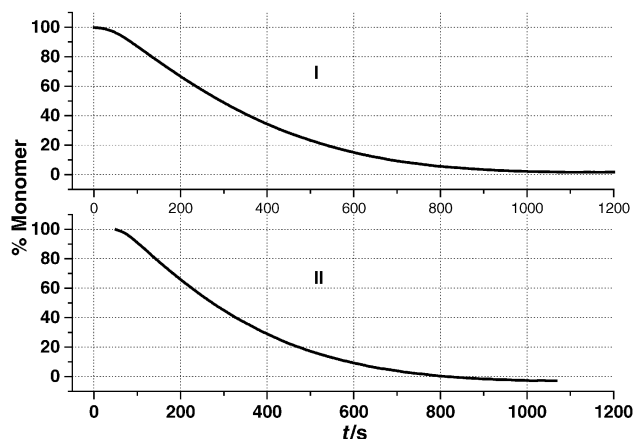


Fig. 9 Reuse. Kinetic data of the first (I) and second (II) reaction. $T_0 = 293 \text{ K}$, 75 ml heptane, 15 ml α -MS. Loading BF_3 : 4 mmol g^{-1} .

weight. Product colour varied from pale to dark yellow. The molecular weight of the polymers were determined by GPC (using low temperature GPC at 40°C with tetrahydrofuran as solvent and a differential refractometer (DRI) and UV-detector) giving values of 1–5K and generally large polydispersities (5–10). The degree of cyclisation was estimated from the degree of unsaturation measured by ^1H NMR intensities of the alkenic proton.

Acknowledgements

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