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Butadiene polymerisation using ternary neodymium-based catalyst systems

The effect of catalyst component addition order

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SUMMARY

Ternary catalyst systems for the polymerisation of 1,3–butadiene to high *cis* content were studied. The systems Nd(carboxylate)$_3$/*tert*–butyl chloride/diisobutylaluminium hydride (carboxylate = naphthenate, versatate) were studied with respect to the order of catalyst component addition on catalyst activity and polymer characteristics. Stable catalysts which give relatively narrow molecular weight distribution are given by component addition order Nd(carboxylate)$_3$ + diisobutylaluminium hydride + *tert*–butyl chloride. Less stable systems giving broader polymer molecular weight distributions are given by addition orders *tert*–butyl chloride + diisobutylaluminium hydride + Nd(carboxylate)$_3$ and Nd(carboxylate)$_3$ + *tert*–butyl chloride + diisobutylaluminium hydride.

INTRODUCTION

Catalysts based on rare earth complexes, in particular those of neodymium, are well known to polymerise 1,3–butadiene to high *cis* content (>98%). A useful review by Marina et. al.(1) covers the literature on rare–earth catalysed polymerisation of dienes up to 1984. Three–component catalyst systems of Nd(carboxylate)$_3$/aluminium alkyl/aluminium alkyl halide or organic halide in a hydrocarbon solvent are perhaps the most useful commercially. These systems tend to be based on naphthenic(2), versatic(3) or octanoic acid(4) salts of neodymium. *Cis* catalysts based on versatic acid with magnesium alkyl and AlEt$_2$Cl have recently been developed(5).

The literature reveals different orders of component addition to form the catalyst premix for the three–component systems mentioned above. Ricci et. al.(4) have followed the order Nd(octanoate)$_3$ + AlEt$_2$Cl + Al(i–butyl)$_3$ and Bayer(3) appear to follow the order Nd(versatate)$_3$ + trialkylaluminium + chloroalkylaluminium. Chinese work(2) has covered both of these orders namely: Nd(naphthenate)$_3$ + Al(i–butyl)$_3$ + Al$_2$Et$_3$Cl$_3$ and Nd(naphthenate)$_3$ + Al$_2$Et$_3$Cl$_3$ + Al(i–butyl)$_3$. The order of addition has been seen to affect the nature of the catalyst(2,4) and the conversion to polymer. In this study the novel system(6) Nd(versatate)$_3$/Al(i–butyl)$_2$H/*tert*–butyl chloride was examined. Observations on the effect of catalyst component addition order on the nature of the catalyst, it's activity and the characteristics of the polymer are discussed.

EXPERIMENTAL

1) Catalyst preparation

Catalysts were prepared(6) in oven dried nitrogen purged crown capped bottles fitted with nitrile rubber liners. Nd(versatate)$_3$ was prepared by the HCl catalysed reaction of Nd$_2$O$_3$ (Rhone–Poulenc) with an excess of versatic acid (Versatic 10, Shell) in hexane. The product was used without isolation. *Tert*–butyl chloride, Al(i–butyl)$_2$H (DIBAL–H) and Nd(versatate)$_3$ were allowed to react together in hexane solvent. All catalysts were prepared with component molar ratio Al:Nd:Cl = 20:1:3.

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a) Sequential Component Addition

Component 2 was added to component 1, and left for 10 min. before adding component 3. For example *tert*-butyl chloride (component 1) + Nd(versatate)$_3$ (component 2) + DIBAL-H (component 3) is denoted Cl + Nd + Al.

b) Premix Component Addition

Component 2 was added to component 1. After 10 min. this mixture was added to component 3 via a double-tipped needle. The above example would be denoted (Cl + Nd) - Al.

2) Polymerisation

Catalyst was injected into bottles charged with 14 wt% 1,3-butadiene in hexane at ambient temperatures to give a catalyst concentration of 0.13mM Nd/100g butadiene. The bottles were then immersed in a water bath at 60°C for different lengths of time. Polymers were terminated after the required time, by venting off excess butadiene and injecting isopropanol/antioxidant. Polymers were dried at 50°C.

3) Characterisation

Conversions were calculated from the % weight of isolated polymer compared to the initial charge of monomer.

Gel permeation chromatography data was obtained from a system employing 4 x 30 cm. Waters Ultrastyragel mixed bed columns with a refractive index detector. THF was used as solvent; flow rate 0.9 ml/min. Polystyrene standards were used to calibrate the system daily. Molecular weights for high *cis* polybutadiene were determined using the universal calibration system. Sample solutions of concentration 0.016% w/v were filtered through a 0.2 μm filter before injection.

RESULTS AND DISCUSSION

Component addition order affected the heterogeneity/instability of the catalyst. Only the order Al + Nd + Cl and Nd + Al + Cl gave catalysts which did not precipitate after 20 hours. Addition orders Nd + Cl + Al and Cl + Nd + Al gave catalysts which formed a precipitate after 20 hours. Addition order Al + Cl + Nd and Cl + Al + Nd gave catalysts which formed a precipitate almost immediately. In general no difference was observed in terms of conversion and polymer characteristics (gpc) if the order of the first two components were reversed (e.g. Al + Nd + Cl versus Nd + Al + Cl). This is illustrated in Figs. 1 & 2.

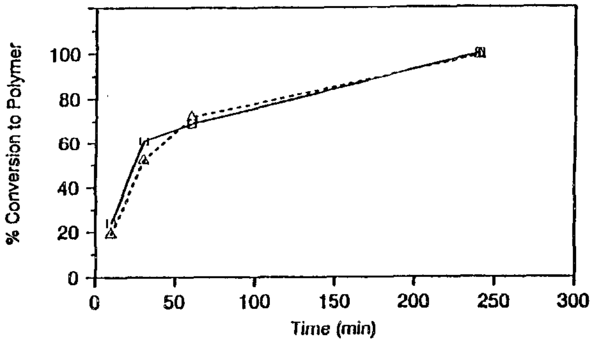

Fig. 1. Variation in conversion to polymer with order of sequential catalyst component addition. Order of addition: Cl + Nd + Al (—□—); Nd + Cl + Al (—Δ—).

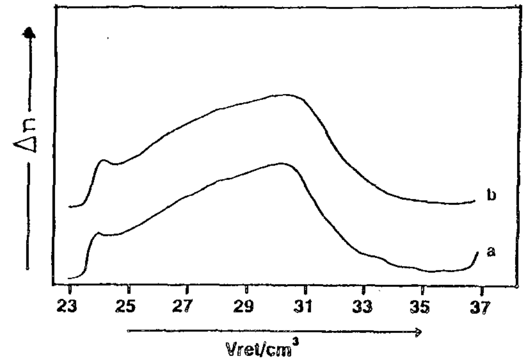

Fig. 2. GPC curves (refractive index difference Δn, versus elution volume) of polybutadiene produced by orders of addition Cl + Nd + Al (a) and Nd + Cl + Al (b) (Fig. 1) at 240 min. polymerisation time.

The addition order Al + Cl + Nd can be compared to the system trialkylaluminium (or dialkylaluminium hydride) + alkylaluminium chloride + $Nd(carboxylate)_3$, which, due to the greater reactivity of alkylaluminium chloride compared to *tert*-butyl chloride, ages rapidly. The heterogeneity of ternary catalysts similar to those studied here, prepared with addition order Nd + Cl + Al are known to be hetergeneous(4).

Polymerisation occuring on the surface of a solid catalyst are rapid. Hence the catalysts examined here with addition order Al + Cl + Nd are very active initially. Initial catalyst activity (i.e. after 10 mins.) folows the order of catalyst heterogeneity i.e. activity Al + Cl + Nd > Nd + Cl + Nd > Al + Nd + Cl (Fig. 3). Two different types of catalyst sites are thought to operate in neodymium-based polymerisations. Initial polymerisation (fast) is believe to occur on insoluble particles which may not be visible to the naked eye(7). Further polymerisation (slow) occurs at the second type of "soluble" catalyst site. As chains grow monomer access to the particle sites is inhibited and chain growth slows. The second (slow) type of chain growth ("soluble") proceeds in a steady quasi-living manner. Thus catalyst activity after longer polymerisation periods (>30 min.) follows the order of catalyst homogeneity i.e. activity Al + Nd + Cl > Nd + Cl + Al > Al + Cl + Nd (Fig. 3). Since rapid polymerisation with highly heterogeneous catalysts will lead to high molecular weight materials, the MWD of polymers produced by such catalysts is somewhat broad (Figs. 4 & 5).

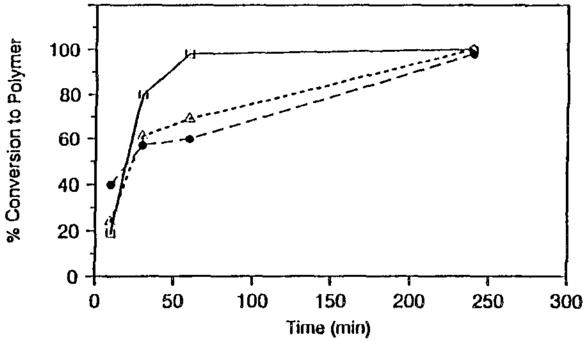

Fig. 3. Variation in conversion to polymer with order of sequential catalyst component addition. Order of addition: Al + Nd + Cl (-□-); Cl + Nd + Al (-▲-); Cl + Al + Nd (-●-).

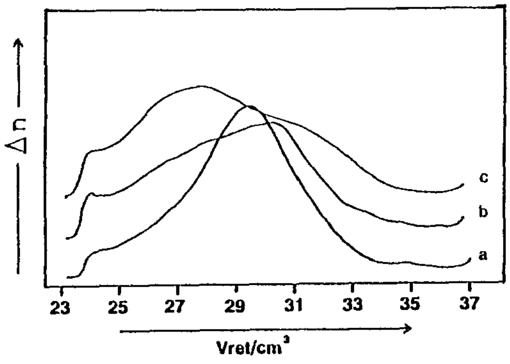

Fig. 4. GPC curves (refractive index difference Δn, versus elution volume) of polybutadiene produced by orders of addition: Al + Nd + Cl (a); Cl + Nd + Al (b) and Cl + Al + Nd (c) at 240 min. polymerisation time.

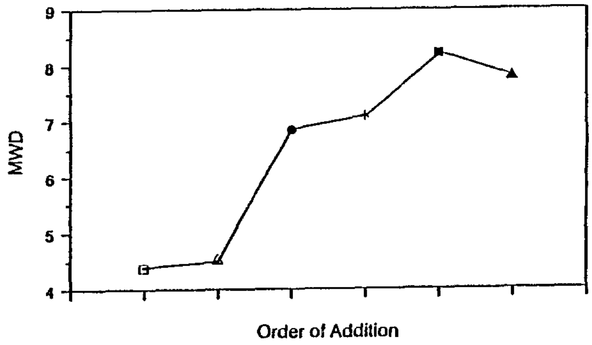

Fig. 5. Polybutadiene MWD vs order of sequential catalyst component addition: Al + Nd + Cl (-□-); Nd + Al + Cl (-△-); Nd + Cl + Al (-●-); Cl + Nd + Al (-✱-); Al + Cl + Nd (-■-); Cl + Al + Nd (-▲-).

b) Premix Component Addition

In general conversions and polymer characteristics were similar to those obtained using sequential component addition i.e. component 1 + component 2 + component 3 = (component 1 + component 2) - component 3. This is illustrated in Figs. 6 & 7.

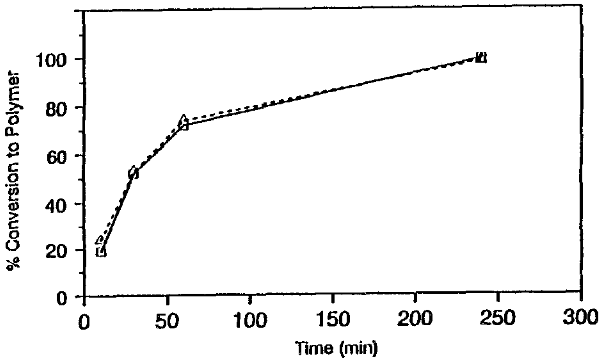

Fig. 6. Variation in conversion to polymer with sequential vs premix catalyst component addition: Nd + Cl + Al (-□-); (Nd + Cl)-Al (-△-).

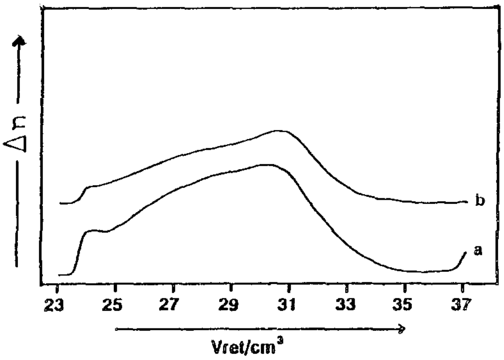

Fig. 7. GPC curves (refractive index difference Δn, versus elution volume) of polybutadiene produced by orders of addition: Nd + Cl + Al (a); (Nd + Cl)–Al (b).

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