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Butadiene polymerisation using ternary neodymium-based catalyst systems

The effect of Nd:halide ratio and halide type

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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 X /diisobutyl aluminium hydride (carboxylate = naphthenate, versatate; X = Cl, Br, I) were studied with respect to the halide:Nd ratio and halide type on catalyst activity and polymer characteristics. A lowering of the halide:Nd ratio results in lower conversions to polymer and a change in polymer molecular weight distribution. Catalyst stability is affected by halide type; instability, or tendency to precipitate, following the order I>Br>Cl. Less active catalysts (e.g. based on *tert*-butyl iodide) give low conversions and broad polymer MWD. *Cis* content remains at 98% and is unaffected by a lowering of halide:Nd ratio or a change in halide type.

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 soluble systems tend to be based on naphthenic (2), versatic (3,4) or octanoic acid (5) salts of neodymium (soluble systems are taken to be those which are clear to the naked eye). *Cis* catalysts based on versatic acid with magnesium alkyl and AlEt$_2$Cl have recently been developed (6). Novel (13) three component soluble catalyst systems based on naphthenic and versatic acid have been examined in a recent paper with respect to the effects of the order of component addition to form the preformed catalyst.(14)

The effect of the Nd:halide molar ratios and type of halide have been examined by various workers for a number of rare-earth catalyst systems involving 1,3-butadiene (1), (3), (4), (7-12). In the present work the novel (13,14) three component soluble catalyst systems described above, namely: Nd(versatate)$_3$ /Al(i-butyl)$_2$H /*tert*-butyl chloride and Nd(naphthenate)$_3$ /Al(i-butyl)$_2$H/*tert*-butyl chloride are examined with respect to the effect of the Nd:halide ratio and type of halide (Cl, Br, I) on conversion of butadiene to polymer and polymer molecular weight distribution. Characterisation of the polymers was carried out using gel permeation chromatography, detailed examples of which are singularly absent from previous work.

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EXPERIMENTAL

Catalyst Preparation

Catalysts were prepared (13) in oven-dried nitrogen-purged crown-capped bottles fitted with nitrile rubber liners. Nd(naphthenate)$_3$ and Nd(versatate)$_3$ were prepared by the HCl catalysed reaction of Nd_2O_3 (Rhone-Poulenc) with an excess of naphthenic acid (Komest) or versatic acid (Versatic 10, Shell) in hexane. The products were used without isolation. *Tert*-butyl chloride (or *tert*-butyl bromide or *tert*-butyl iodide), Al(i-butyl)$_2$H (DIBAL-H) and Nd(naphthenate or versatate)$_3$ were allowed to react together in hexane solvent. A catalyst of component molar ratio Al:Nd:Cl=20:1:3 was used as control.

Polymerisation

Catalyst was injected into bottles charged with 14 wt% 1,3-butadiene in hexane at ambient temperature 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 in *vacuo*.

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 30cm Water 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.

Cis contents of the polymers were measured by infra-red spectroscopy.

RESULTS AND DISCUSSION

Catalysts

Catalysts based on *tert*-butyl chloride are soluble. Those based on *tert*-butyl bromide give some precipitate after 20 hours. Catalysts based on *tert*-butyl iodide give a heavy precipitate almost immediately. The tendency towards heterogeneity or instability of the catalyst system i.e. the tendency to precipitate follows the order of decreasing electronegativity of the halide involved i.e. Cl("homogeneous")>Br> I("heterogeneous").

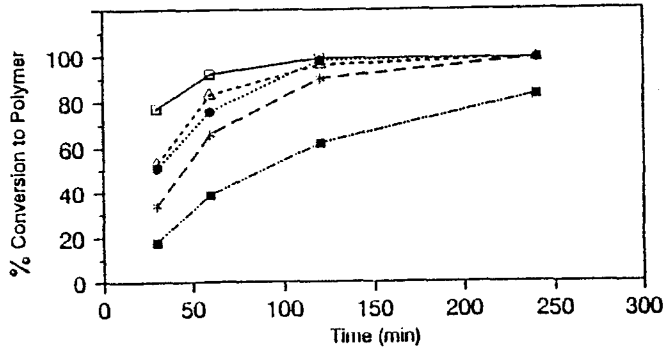

FIG 1. Nd:Cl molar ratio vs conversion to polymer for Nd(versatate)$_3$-based catalysts. Nd:Cl ratio: 1:3 (— □ —); 1:2.5 (— Δ —); 1:2 (— ● —); 1:1.5 (— * —); 1:1 (— ■ —).

Catalyst activity

The effects on conversion of a decrease of Cl:Nd ratio for Nd(versatate)$_3$ and Nd(naphthenate)$_3$-based catalysts are shown in Figs. 1 & 2. A lower Cl:Nd ratio gives lower rates of conversion to polymer for both Nd(versatate)$_3$ and Nd(naphthenate)$_3$-based catalysts since fewer catalyst sites will be created when less Cl is used. Nd(versatate)$_3$-based catalysts are more active then Nd(naphthenate)$_3$-based catalysts. This may be due in part to the more reactive carboxyl group in Versatic 10 (neodecanoic acid, alpha-branched).

Catalysts prepared using *tert*-butyl bromide as halide give similar rates of conversion to those based on *tert*-butyl chloride at the same halide:Nd ratio (Fig. 3 & 4). Catalysts based on *tert*-butyl iodide give much lower rates of conversion than catalysts based on *tert*-butyl chloride and *tert*-butyl bromide (Fig. 5 & 6). With a highly heterogeneous catalyst based on *tert*-butyl iodide, high molecular weight material is formed rapidly on the particle surface; this slows as monomer access to the surface site becomes inhibited with resultant low conversion. The catalyst activity with variation in halide type follows the order Cl>Br>>I.

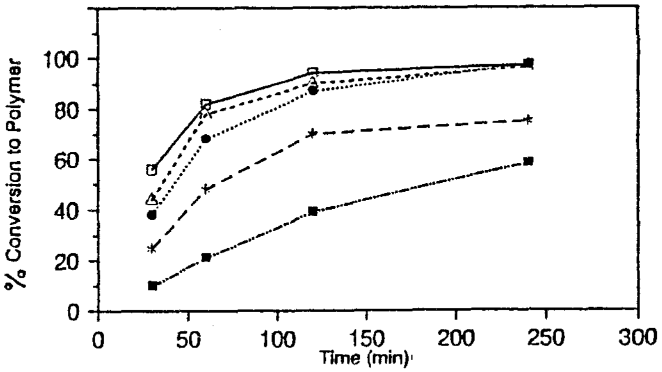

FIG 2. Nd:Cl molar ratio vs conversion to polymer for Nd(naphthenate)$_3$ -based catalysts. Nd:Cl ratio: 1:3 (— □ —); 1:2.5 (— Δ —); 1:2 (— ● —); 1:1.5 (— * —); 1:1 (— ■ —).

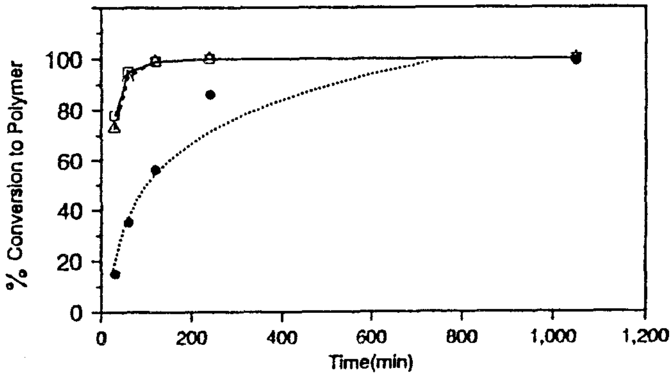

FIG 3. Halide type vs conversion to polymer for Nd(versatate)$_3$-based catalysts (Cl vs Br). Nd:Cl ratio 1:3 (— □ —), Nd:Br ratio 1:3 (— Δ —), Nd:Br ratio 1:1 (— ● —).

Polymer characterisation

Polybutadiene prepared using Al(i-butyl)$_2$H and alkyl halide as components of rare-earth catalysts is typically bimodal at low conversions, whereas at high conversions the product is almost monomodal with a shoulder on the high molecular weight side. Two different catalyst sites are believed to be held responsible for this phenomenon. Initial polymerisation (fast) is thought to occur at one type of site. This rapid initial polymerisation leading to high molecular weight material, may occur on insoluble particles which are not visible to the naked eye (15). Further polymerisation (slow) occurs at the second type of "soluble" catalyst site.

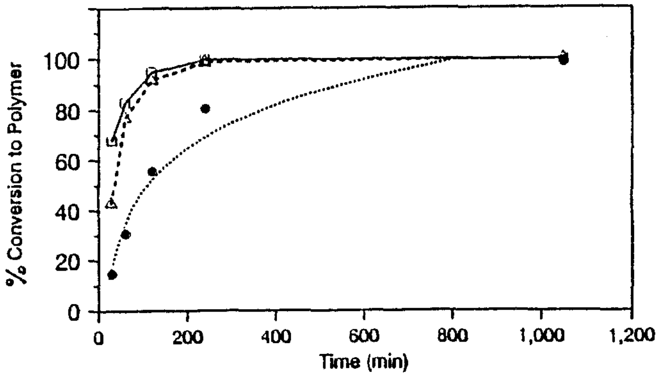

FIG 4. Halide type vs conversion to polymer for Nd(naphthenate)$_3$-based catalysts (Cl vs Br). Nd:Cl ratio 1:3 (— □ —), Nd:Br ratio 1:3 (— Δ —), Nd:Br ratio 1:1 (— ● —).

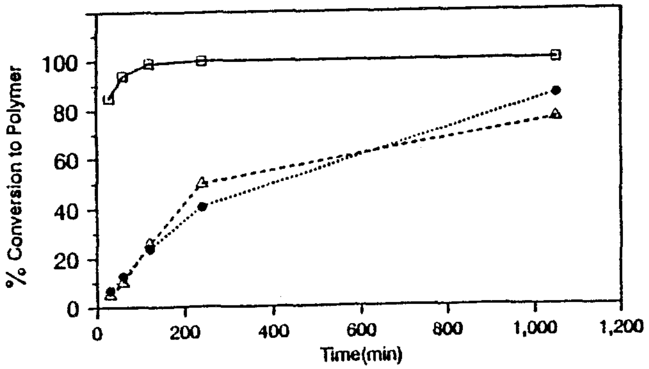

FIG 5. Halide type vs conversion to polymer for Nd(versatate)$_3$-based catalysts (Cl vs I). Nd:Cl ratio 1:3 (— □ —), Nd:I ratio 1:3 (— Δ —), Nd:I ratio 1:1 (— ● —).

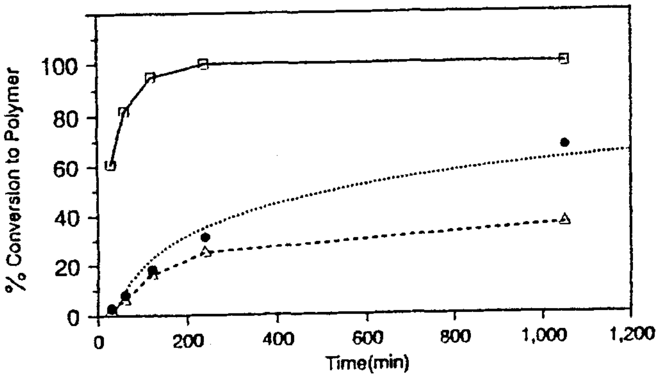

FIG 6. Halide type vs conversion to polymer for Nd(naphthenate)$_3$-based catalysts (Cl vs I). Nd:Cl ratio 1:3 (— □ —), Nd:I ratio 1:3 (— Δ —), Nd:I ratio 1:1 (— ● —).

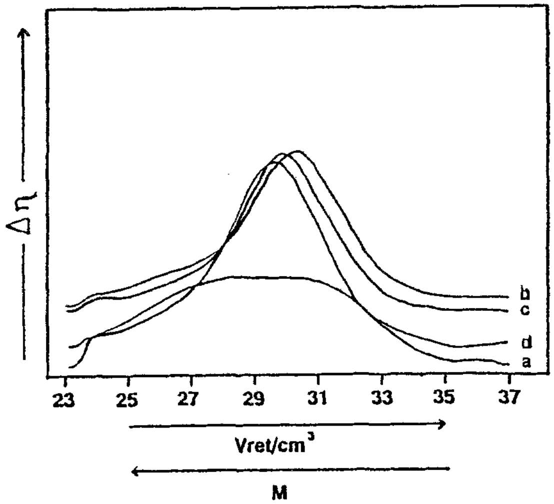

FIG 7. GPC curves (refractive index difference Δη, versus elution volume) of polybutadiene produced for different polymerisation times using a Nd(versatate)$_3$-based catalyst: 10 min(a); 30 min (b); 60 min (c); 120 min (d).

Fig. 7 shows clearly the change in proportion of high molecular weight material as the polymerisation proceeds. Initial high molecular weight material is formed on the insoluble particle sites. As chains grow monomer access is inhibited. The second (slow) type of chain growth ("soluble") proceeds in a steady *quasi*-living manner. As a result the original high molecular weight material is barely seen at full conversion. The effect of a lowering of Cl:Nd ratio on molecular weight distribution (MWD) of polymer (full conversion) catalysed by Nd(versatate)$_3$ and Nd(naphthenate)$_3$-based systems is shown in Fig. 8. In general, MWD values of polymer produced from Nd(versatate)$_3$ and Nd(naphthenate)$_3$ catalyst system exhibit roughly the same trend with a change in Cl:Nd ratio. At low Cl:Nd ratios (1:1) MWD is broad due to the lower number of active "soluble" sites relative to insoluble particle sites producing high molecular weight polymer. Broad MWD at high Cl:Nd ratios (3:1) may result from "overchlorination" of catalyst sites. Although the relationship between Cl:Nd ratio and MWD is not linear, for both systems the Cl:Nd ratio of 2–2.5 tends to give the product with the narrowest MWD. The tendency of catalysts based on *tert*–butyl bromide to heterogeneity is reflected in the broader MWD of the polymer obtained as shown in Fig. 9 which compares products obtained at the same conversion (76%) using a *tert*–butyl chloride–based catalyst a *tert*–butyl bromide–based catalyst and a *tert* butyl–iodide–based catalyst.

The highly heterogeneous catalysts formed using *tert*–butyl iodide as halide source produce polybutadiene with has a high molecular weight and a very broad MWD. As seen in Fig. 10, high molecular weight material is always predominant.

Cis contents of the polymers isolated after 4 hours polymerisation time at halide:Nd ratios of 1:3 and 1:1 using tert–butyl chloride, bromide and iodide remained at 98%.

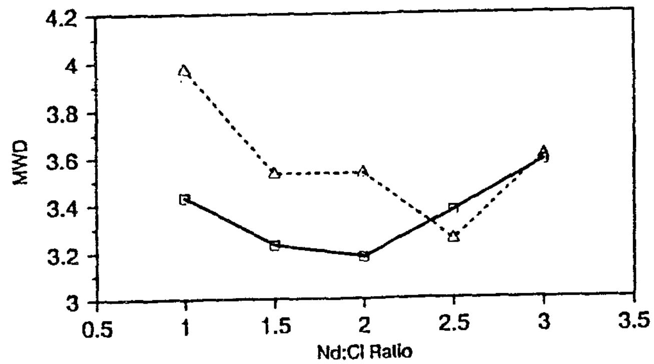

FIG 8. Nd:Cl ratio vs polybutadiene MWD for Nd(versatate)$_3$ (— □ —) and Nd(naphthenate)$_3$ (— Δ —)–based catalysts.

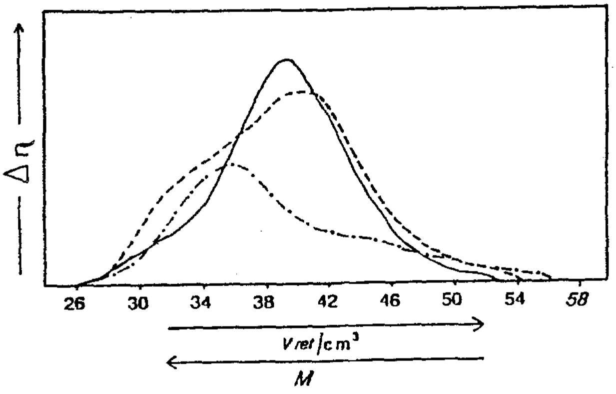

FIG 9. GPC curves (refractive index difference Δη, versus elution volume) of polybutadiene produced using Nd(versatate)$_3$–based catalysts. halide: Cl (————); Br (– – – – –); I (–·–·–·–), Nd:halide ratio 1:3.

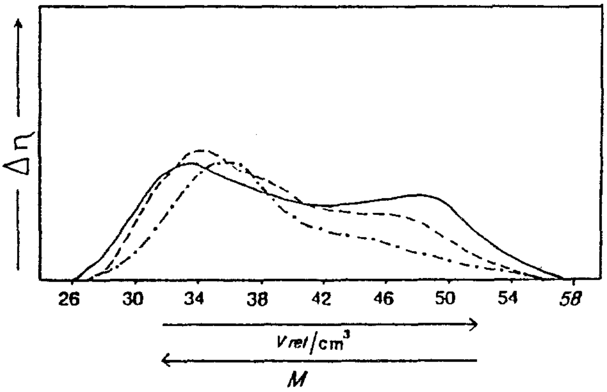

FIG 10. GPC curves (refractive index difference Δη, versus elution volume) of polybutadiene produced using Nd(versatate)$_3$/*tert*-butyl iodide-based catalyst. Polymerisation time: 1 hour (————); 4 hours (– – – – –); 17.5 hours (–·–·–·–).

CONCLUSIONS

A change in the Cl:Nd catalyst component ratio for the high *cis* polybutadiene catalyst systems studied, effects the conversion to polymer and the MWD of the polymer. This is due to the number and nature of the catalyst sites created. A change in the halide catalyst component leads to unstable catalysts with decreasing electronegativity of the halide. The tendency of the catalysts to precipitate is reflected in their lower activity and broader MWD values. Polymer *cis* content is unaffected by halide:Nd ratio or halide type.

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