A rare earth catalyst system for the polymerization of 1,3-butadiene: the effect of different carboxylates

David J. Wilson
R&D Laboratory, Enichem Elastomers Ltd, Bo'ness Road, Grangemouth, Stirlingshire, FK3 9XE, UK

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Ternary neodymium-based catalysts of the form Nd(carboxylate)$_3$/Al(i-butyl)$_2$H/^{tert}butyl chloride for the high-*cis* polymerization of 1,3-butadiene have been examined. The carboxylates of a range of neo and iso monocarboxylic acids have been used and their effects on catalyst activity and polymer molecular weight examined. Catalysts prepared using neoacids are more active and give lower molecular weight polymer than catalysts prepared using isoacids. Increasing the chain length of carboxylic acid gives more active catalysts; this trend is more prominent within the isoacids than the neoacids. Increased catalyst activity is explained in terms of the changing nature of the Nd–O bond in the Nd(carboxylate)$_3$ and the ease of alkylation in the formative step of catalyst active site creation.

(Keywords: neodymium; 1,3-butadiene; high *cis*; carboxylic acid)

INTRODUCTION

Catalysts based on rare earth metals, notably neodymium, are capable of polymerizing 1,3-butadiene to high *cis* content (>98%). Marina *et al.*[1] have reviewed the literature of the rare-earth-catalysed polymerization of dienes up to 1984. The physical properties of high-*cis* polybutadiene prepared using neodymium-based catalysts are superior to those of material prepared using conventional transition metal catalyst systems[2]. 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 for the solution polymerization of 1,3-butadiene. These are normally regarded as soluble systems (soluble indicating clear to the naked eye). Recently the novel[3] catalyst system Nd(carboxylate)/Al(i-butyl)$_2$H/^{tert}butyl chloride has shown promise in the preparation of high-*cis* polybutadiene[4].

A relatively restricted range of carboxylic acids for use in these catalyst preparations have been examined in the literature. The systems are generally based on naphthenic[5], versatic (Versatic 10)[6,7] or 2-ethyl hexanoic (octanoic)[8] acid salts of neodymium. There are, however, disadvantages to some of these acids. Naphthenic acid, a crude oil fraction, is highly variable in composition[9] and solutions of neodymium salts of 2-ethyl hexanoic acid are rather viscous even at high dilution[10]. In this work the catalyst system Nd(carboxylate)$_3$/Al(i-butyl)$_2$H/^{tert}butyl chloride was examined, in which the carboxylate was derived from a range of commercially available monocarboxylic acids. Since neodymium salts of linear monocarboxylic acids display poor solubility in aliphatic solvents, only branched acids were examined. Acids used were neocarboxylic acids (neoacids), isocarboxylic acids (isoacids) and mixtures. Neoacids are based on a trialkylacetic acid structure (alpha carbon branching) whereas isoacids have a branched structure whose predominant isomer is non-alpha branched.

EXPERIMENTAL

Catalyst preparation

Catalysts were prepared[3] in oven-dried nitrogen-purged crown-capped bottles fitted with nitrile rubber liners. Nd(carboxylate)$_3$ was prepared by the HCl-catalysed reaction of Nd_2O_3 (Rhône-Poulenc) with an excess of the carboxylic acid in hexane. The Nd(carboxylate)$_3$ product was used without isolation. ^{tert}Butyl chloride, Al(i-butyl)$_2$H and Nd(carboxylate)$_3$ were allowed to react together in hexane solvent. Catalyst component molar ratio was Al:Nd:Cl = 20:1:3. Catalysts based on Versatic 10 were used as the control.

Carboxylic acids

The carboxylic acids used were obtained as free samples from Shell Chemicals Ltd, Exxon Chemical Ltd and Hoechst UK Ltd. Shell supplied the following: neoheptanoic acid (Versatic 7, 95% 2,2-dimethylpentanoic acid, 5% 2,2-dimethyl butanoic acid); neononanoic acid (Versatic 9); neodecanoic acid (Versatic 10); neotridecanoic acid (Versatic 13); neodecanoic, neononadecanoic acid mixture (Neo 1019, 85% neononadecanoic acid). Exxon supplied the following: isoheptanoic acid (Cekanoic C7); isotridecanoic acid (Cekanoic C13); neononanoic, neodecanoic acid mixture (Neo 910, 90% purity, 67% neodecanoic, 23% nonanoic acid). Hoechst supplied the following: isooctanoic (99% purity, isomer mixture, isomer proportions unknown); isononanoic acid (99% purity, isomer mixture, >90% 3,5,5-trimethylhexanoic acid); isodecanoic acid (99% purity, isomer mixture, isomer proportions unknown).

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Polymerization

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

Polymer characterization

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

Isomer content. The %*cis*, %*trans* and %vinyl contents of the polymers were measured by an i.r. method. A Perkin–Elmer 377 grating i.r. spectrophotometer operating in absorbance mode was used. Films were cast from cyclohexane solution onto KBr plates. Isomer absorbance occurs at 724.6 cm^{-1} (*cis*), 961.5 cm^{-1} (*trans*) and 909.1 cm^{-1} (vinyl). The extinction coefficients used were 0.6080 (*cis*), 2.61 (*trans*) and 3.285 (vinyl).

Gel permeation chromatography. Gel permeation chromatography (g.p.c.) data were obtained from a Shimadzu system. A Shimadzu RID-6A refractive index detector, LC-6A pump and C-R4A chromatopac data processor were used. Waters Ultrastyragel columns 3 × THF Linear and one 10^6 Å were used in a Shimadzu CTO-6A column compartment maintained at 35°C. Tetrahydrofuran was used as solvent; flow rate 0.9 ml min^{-1}. Polystyrene standards (Polymer Laboratories) were used to calibrate the system daily. Molecular weights for high-*cis* polybutadiene were determined using the universal calibration system; Mark–Houwink values used for high-*cis* polybutadiene were $K = 4.57 \times 10^{-4}$, $a = 0.693$. Sample solutions of concentration 0.016% w/v were filtered through a 0.2 μm filter before injection. The exclusion limit of this particular column set was of the order of 10^5 as polybutadiene.

Mooney viscosity. Mooney viscosity measurement was carried out on a Negretti Automation Mooney Viscosimeter. This simple rotational instrument is commonly used in the rubber industry and measures the torque required to revolve a rotor at constant speed in a sample of polymer at constant temperature. Upper and lower plates were maintained at 100°C. The equipment was calibrated on a regular basis using a sample of high-*cis* polybutadiene of Mooney viscosity 40.

RESULTS AND DISCUSSION

Neodymium salts of the isoacids examined were not completely soluble in hexane, displaying a slight turbidity which persisted even after decantation. Salts of the neoacids, however, gave clear solutions in hexane. The solubility of neodymium salts of monocarboxylic acids in hexane follow the order neoacid > isoacid > linear acid. It was found that for neodymium salts of iso- and neoacids in hexane, solubility occurs if the main chain is five or more carbon atoms long and the chain is methyl branched. For example, the neodymium salts of 2,2-dimethyl propanoic acid (pivalic or Versatic 5 acid), 2,2-dimethyl butanoic acid (Versatic 6) and 2-ethyl-2-methyl butanoic acid (one of two commercially available Versatic 7 products) are insoluble in hexane. The neodymium salts of most linear monocarboxylic acids are insoluble in hexane.

The activities of catalysts based on the isoacids studied are shown in *Figure 1*. There is a clear indication that catalyst activity increases with an increase in the chain length of the isoacid. This is exemplified in *Figure 2*, where relative catalyst activity is plotted against carboxylic acid chain length for 30 and 60 min polymerization time. When considering this increase in catalyst activity with increased carboxylic acid chain length we must consider the changing nature of the Nd–O bond in the $Nd(carboxylate)_3$. Increasing chain length of carboxylic acid may lead to weaker acids resulting in the Nd–O bond becoming progressively more covalent. This facilitates the alkylation of the $Nd(carboxylate)_3$ by the aluminium alkyl, the primary step in the creation of the active centres. However, when considering the nature of the $Nd(carboxylate)_3$ in hexane, solvation, steric effects and entropy considerations must be taken into account. Although the neodymium carboxylates of all these isoacids appeared to be equally soluble in hexane, the lower solubility of Nd carboxylates of shorter chain acids must hamper the alkylation step and thus play a part in the reduced activity of the subsequent catalyst.

The activities of catalysts based on neoacids are shown in *Figures 3* and *4*. As for isoacids, the activity of catalysts

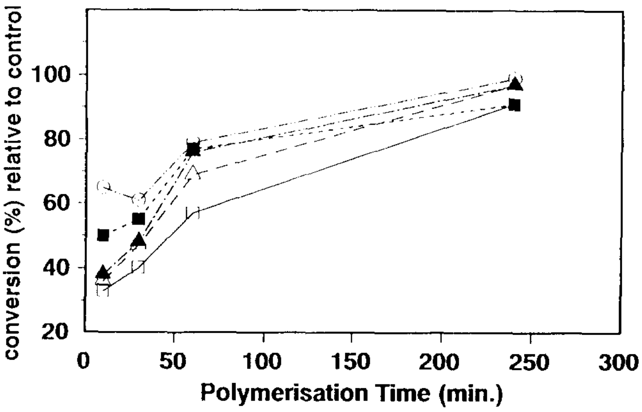

Figure 1 Comparison of polymerization activity of catalysts prepared using different isoacids. □, Isoheptanoic acid; △, isooctanoic acid; ■, isononanoic acid; ▲, isodecanoic acid; ○, isotridecanoic acid

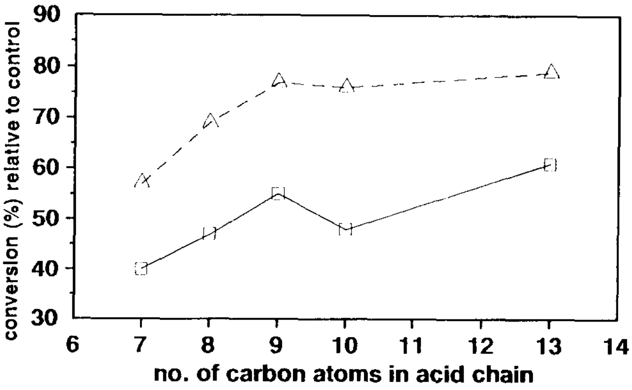

Figure 2 Comparison of polymerization activity of catalysts prepared using different isoacids as in *Figure 1* at 30 min (□) and 60 min (△) polymerization time

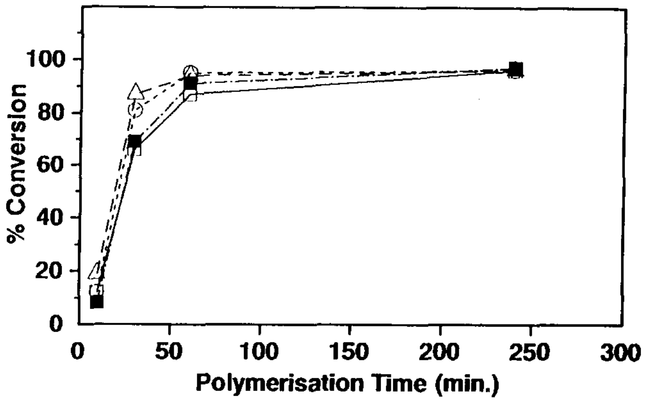

Figure 3 Comparison of polymerization activity of catalysts prepared using different neoacids. □, Neoheptanoic acid; △, neononanoic acid; ○, neodecanoic acid; ■, neotridecanoic acid

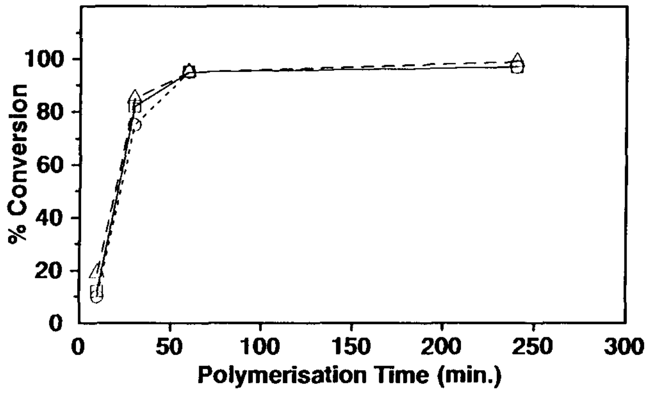

Figure 4 Comparison of polymerization activity of catalysts prepared using different neoacid mixtures. □, Neodecanoic acid control; △, neononanoic/neodecanoic acid mixture; ○, neodecanoic/neononadecanoic acid mixture

prepared using neoacids appears to depend on the chain length of the original carboxylic acid, but the situation is not quite as clear. As seen in *Figure 3*, catalysts based on neoheptanoic acid are lowest in activity (the activity of catalysts prepared using neononanoic and neodecanoic acid are roughly equivalent). However, catalysts prepared using neotridecanoic acid are also low in activity. This is also seen in *Figure 4*, where a catalyst prepared using a mixture of longer chain acids (neodecanoic and neononadecanoic acid) is lower in activity than the neodecanoic acid control. For catalysts prepared from neoacids there appears to be a limiting carboxylic acid chain length at around 10 carbon atoms after which catalyst activity is reduced.

Catalysts based on neoacids are more active compared to their isoacid counterparts. *Figure 5* illustrates this situation for neodecanoic and isodecanoic acids. The reasons for the enhanced activity of catalysts prepared using isoacids with increasing chain length would go some way to explaining the higher activity found by catalysts based on neoacids compared to isoacids. Neocarboxylic acids are based on a trialkylacetic acid structure (alpha carbon branching) whereas isoacids have a branched structure whose predominant isomer is non-alpha branched. The increased substitution of the neoacids makes them weaker acids, facilitating alkylation of the Nd(carboxylate)$_3$ as described above. The superior solubility in aliphatic hydrocarbons of the neoacid-based Nd carboxylates over those of the isoacids will, in addition, render faster and more complete alkylation, resulting in a more active catalyst species.

One of the characteristics of the stereospecific polymerization of conjugated dienes by neodymium-based catalysts is the 'quasi-living' nature of the system. When conventional transition metal systems for the polymerization of dienes are used (Ti-, Co- and Ni-based systems) the molecular weight attains a maximum at about 40% conversion due principally to chain transfer to monomer. When neodymium-based systems are used, molecular weight continues to grow in a semi-regular fashion, and an approximate first-order reaction with respect to monomer is observed. A plot of $-\ln(1-\text{fractional conversion})$ *versus* polymerization time for the catalyst system based on isodecanoic/neodecanoic acids is shown in *Figure 6*. The system shows a respectable linear relationship between $-\ln(1-\text{fractional conversion})$ and polymerization time. It is especially true for the isodecanoic acid system.

The g.p.c. data for all the polymerization systems examined are shown in *Table 1*. Catalysts prepared using isoacids are less active in the polymerization of 1,3-butadiene than those prepared using neoacids, presumably due to the lower number of catalytically active centres created as a result of the considerations previously described. Since a 'quasi-living' mechanism is seen to operate, this naturally leads to higher-molecular-weight polymer at high conversion when using catalysts prepared from isoacids compared to neoacids. This is

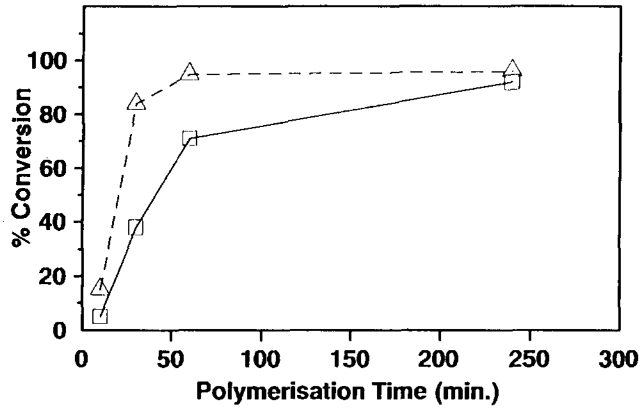

Figure 5 Comparison of polymerization activity of catalysts prepared using isodecanoic acid (□) and neodecanoic acid (△)

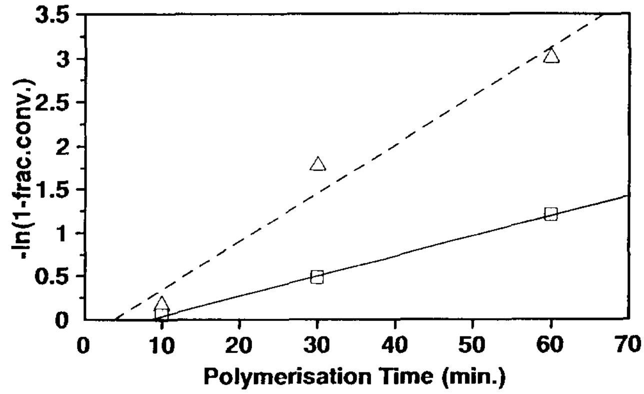

Figure 6 Plot of $-\ln(1-\text{fractional conversion})$ *versus* polymerization time for data from *Figure 5*: □, isodecanoic acid-based catalyst; △, neodecanoic acid-based catalyst

Table 1 G.p.c. data for polybutadiene prepared from catalysts derived from different carboxylic acids

Acid	Polymerization time (min)	M_n $\times 10^{-3}$	M_w $\times 10^{-3}$	M_{peak} $\times 10^{-3}$	*MWD*
Neo 7	10	57	511	62	9.03
	30	99	398	150	4.00
	60	138	457	204	3.32
	240	152	512	250	3.39
Neo 9	10	76	478	60	6.32
	30	110	396	115	3.60
	60	129	422	139	3.28
	240	151	480	191	3.18
Neo 10	10	73	525	60	7.16
	30	101	350	117	3.45
	60	119	380	133	3.21
	240	147	466	195	3.18
Neo 13	10	112	692	139	6.18
	30	141	502	197	3.56
	60	165	561	244	3.49
	240	200	607	279	3.03
Neo 9/10	10	65	391	53	6.04
	30	107	328	149	3.06
	60	151	454	232	3.01
	240	133	433	223	3.26
Neo 10/19	10	101	592	74	5.84
	30	126	445	142	3.54
	60	128	416	169	3.25
	240	138	438	210	3.18
Iso 7	10	179	718	145	4.00
	30	158	599	229	3.78
	60	201	693	300	3.44
	240	269	871	411	3.24
Iso 8	10	170	694	128	4.07
	30	193	677	329	3.51
	60	189	760	430	4.03
	240	269	919	506	3.43
Iso 9	10	148	632	152	4.28
	30	177	625	270	3.53
	60	202	677	340	3.36
	240	310	999	497	3.23
Iso 10	10	117	657	787	5.63
	30	140	513	184	3.66
	60	177	605	285	3.42
	240	268	879	463	3.28
Iso 13	10	80	396	71	4.91
	30	116	398	146	3.43
	60	141	474	222	3.36
	240	188	616	325	3.27

seen in *Table 1* on inspection of M_{peak} values obtained from g.p.c. measurements of polymers obtained after 4 h polymerization time. If we compare catalysts prepared using either neoacids or isoacids, polybutadiene prepared from catalysts using isoacids are markedly higher in molecular weight than those obtained using neoacids. The molecular weight distributions (*MWD*s) of these 4 h polymers are also shown in *Table 1*. There is no obvious trend in *MWD* with molecular weight for these 4 h polymers or with the type of carboxylic acid used in the catalyst preparation, and the polymer *MWD* values remain fairly constant irrespective of the type of carboxylic acid used; an average *MWD* of 3.25 with a deviation of 12% is observed over the whole range of acids. Broad polymer *MWD*s, tending towards bimodality at the onset of polymerization and becoming narrower as polymerization continues, were observed for all these systems (*Table 1*). This phenomenon has been documented for both 'preformed' and *in situ*-prepared rare earth catalyst systems[2,11] and is thought to arise from the presence of two different types of active catalyst site, one of which is longer lived. Neodymium-based catalyst systems, similar to those reported here but differing in component addition order[4], may form insoluble material whilst remaining active; the *MWD*s of polymers obtained using these catalysts are broad. The soluble catalysts reported in the present work may therefore contain insoluble material not visible to the naked eye where initial polymerization leading to high-molecular-weight material occurs. As chains grow at these sites, monomer access is inhibited. The second (slow) type of chain growth occurs at soluble catalyst sites and proceeds in a 'quasi-living' manner. As a result, at low conversions to polymer a greater proportion of high-molecular-weight material is present and the *MWD* of the polymer is broad.

Mooney viscosity measurements reflect large changes in molecular weight. *Figure 7* shows a plot of catalyst concentration *versus* Mooney viscosity of polymers obtained after 4 h polymerization time for catalysts based on neodecanoic acid and a neodecanoic/neononadecanoic acid mixture. The activities of the two systems are similar (*Figure 4*) and this is reflected in the close agreement of Mooney viscosity values throughout the catalyst range examined (*Figure 7*).

The 1,4-*cis* isomer content in polybutadiene prepared by the use of neodymium-based catalysts remains the same (98%) over a wide range of catalyst systems[1],

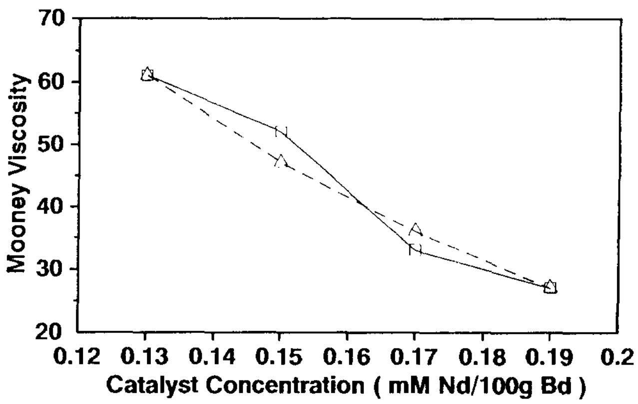

Figure 7 Mooney viscosity *versus* catalyst concentration for polymers obtained after 4 h polymerization time. Catalysts prepared using neodecanoic acid (□) and a neodecanoic/neononadecanoic acid mixture (△)

Table 2 Microstructure for polymers obtained after 4 h polymerization time, using different isoacids, neoacids and mixtures in the catalyst preparation

Acid	%*cis*	%*trans*	%vinyl
Neo 7	98.4	1.4	0.2
Neo 9	98.4	1.2	0.4
Neo 10	98.5	1.1	0.4
Neo 13	98.4	1.1	0.5
Neo 9/10	98.2	1.2	0.6
Neo 10/19	98.9	0.7	0.4
Iso 7	98.9	0.8	0.3
Iso 8	98.8	0.6	0.6
Iso 9	98.7	0.5	0.8
Iso 10	98.7	0.7	0.6
Iso 13	99.0	0.5	0.5

unlike conventional transition metal systems[12–14]. The microstructure of polybutadiene obtained after 4 h polymerization time using catalysts prepared from the range of acids examined is shown in *Table 2*. It is seen quite clearly that the *cis* content is unaffected by the type of carboxylic acid used in the catalyst preparation.

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