changes in polar networks may influence r_o^2 not only due to the volume difference of the rotational isomers but also because of the pressure variation of dielectric interactions.

The illustrative calculation confirms that even a minute change of reference chain dimensions with pressure has an important outcome for thermodynamic analysis of rubber elasticity. As was pointed out by Staverman[3] this effect is important even though the macroscopic volume changes of the sample during deformation can safely be neglected. The postulate about the exclusively intramolecular origin of rubber elasticity is invalidated in networks under strong pressure where the intermolecular packing and steric forces play a significant role and thermodynamic relations for the force f have to be modified by additional term containing parameter γ[1,2,15]. Further, the results indicate the necessity of more detailed investigation of pressure-volume configurational properties of polymer chains unperturbed by long-range interactions. Neglect of the pressure or volume as variables in chain statistics might not be so warranted as is generally believed. Finally, it should be pointed out that similar reasoning as presented above can also be invoked in explanation of the change in polymer conformation with pressure in amorphous glassy polymers[16].

References

1 Tobolsky, A. V. and Shen, M. *J. Appl. Phys.* 1966, **37**, 1952
2 Shen, M. and Croucher, M. *J. Macromol. Sci.-Revs.* 1975, **C12**, 287
3 Staverman, A. J. *J. Polym. Sci.* 1975, **37**, 1952
4 Bleha, T. *Makromol. Chem., Rapid Commun.* 1981, **2**, 35
5 Bleha, T., Gajdos, J. and Tvaroska, I. *J. Molec. Struct.* 1980, **68**, 189
6 Shoen, P. E., Priest, R. G., Sheridan, J. P. and Schnur, J. P. *J. Chem. Phys.* 1979, **71**, 317
7 Flory, P. J. Statistical Mechanics of Chain Molecules, Interscience, New York, N.Y., 1969
8 Hammel, G. L., Schulz, G. V. and Lechner, M. D. *Eur. Polym. J.* 1979, **15**, 209
9 Gaeckle, D. and Patterson, D. *Macromolecules* 1972, **5**, 136
10 Kubota, K., Kubo, K. and Ogino, K. *Bull. Chem. Soc. Japan* 1976, **49**, 2410
11 Wolf, F. P. and Allen, G. *Polymer* 1975, **16**, 209
12 Sharda, S. C. and Tschoegl, N. W. *Macromolecules* 1976, **9**, 910
13 Godovsky, Yu. K. *Polymer* 1981, **22**, 75
14 Patterson, M. S. J. Appl. Phys., 1964, **35**, 176
15 Vasko, M., Bleha, T. and Romanov, A. *J. Macromol. Sci.-Revs.* 1976, **C15**, 1
16 O'Reilly, J. M. and Mosher, R. A. *J. Polym. Sci., Polym. Lett. Edn.* 1979, **17**, 731

Block copolymers synthesis *via* anionic to Ziegler–Natta transformation reaction

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Introduction

A new approach has been developed in recent years to the synthesis of block copolymers involving novel combinations of monomers. This has required devising transformation reactions to enable the mode of polymerization employed for the first monomer to be switched to a different mode most suitable for polymerizing a second monomer. Such processes require an intermediate stage where the initial homopolymer may be isolated before being introduced into an environment appropriate to the polymerization of the second monomer. Examples have been published of the following transformation reactions: anion to cation[1–4], anion to free radical[5–8], and cation to anion[9], and the subject has been recently reviewed[10]. Other transformations are currently being studied, and this publication is a preliminary report of an approach to the transformation from anion to Ziegler–Natta (ZN) catalysis.

ZN catalytic systems were defined as a combination of metal alkyls of Groups I to III with transition metal salts of Groups IV to VIII[11,12]. In practice, very efficient catalyst combinations are derived from the interaction of aluminium or lithium alkyls with titanium, vanadium or cobalt salts, and in this study, investigation has been confined to catalysts involving titanium III or IV as a component.

The classical interpretation of the mode of reaction between aluminium alkyl and a titanium IV salt is initially one of reduction of the latter to titanium III (equations 1 and 2), the alkyl radical generated being eliminated by termination.

$$\mathrm{TiCl_4 + R_3Al \rightarrow RTiCl_3 + R_2AlCl} \qquad (1)$$

$$\mathrm{RTiCl_3 \rightarrow \beta TiCl_3 + R\cdot} \qquad (2)$$

Further alkylation of the titanium III salt then occurs to generate the titanium species capable of initiating polymerization of monomers such as ethylene (equations 3 and 4). When the alkyl group is small (e.g. ethyl), such catalytic systems are insoluble in normal solvents such as hexane, but increase in the size of the ligand leads to increased solubility with retention of catalytic activity[13]. An analogous set of reactions applies to the formation of catalysts from the interaction of lithium alkyls and titanium salts.

$$\mathrm{\beta TiCl_3 + R_3Al \rightarrow RTiCl_2 + R_2AlCl} \qquad (3)$$

$$\mathrm{RTiCl_2 + C_2H_4} \underset{\text{coordination}}{\rightarrow} \mathrm{RTiCl_2.C_2H_4} \underset{\text{insertion}}{\rightarrow} \mathrm{RCH_2CH_2TiCl_2} \qquad (4)$$

Since the alkyl ligand is incorporated in the final polymer produced (equation 4), it seemed feasible that the

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polymerization systems outlined above could be adapted to effect an anion to ZN transformation process in order to prepare novel block copolymers. Thus lithium living polymers could be used in lieu of lithium alkyls — such combinations, used to examine the effect of alkyl size on catalyst solubility, had already shown catalytic activity[13] —and polymer–aluminium derivatives could be prepared to replace the small molecule aluminium alkyls in ZN catalyst combinations. The latter derivatives could be synthesized by successive alkylation of aluminium halides with living anionic polymers (equation 5).

$$AlCl_3 + Pol^-Li^+ \rightarrow Pol\,AlCl_2 + Pol^-Li^+ \rightarrow (Pol)_2AlCl + Pol^-Li^+ \rightarrow (Pol)_3Al \qquad (5)$$

This communication gives a preliminary report on the products obtained from the polymerization of ethylene using such catalysts and assesses relative efficiencies of these catalysts in the formation of block copolymer.

Experimental

Materials. The purification of isoprene, styrene and solvents to the standards required for ionic polymerization has been described in previous publications[15–18].

Techniques. Previous publications[15–18] also outline the experimental procedures involving greaseless high vacuum systems and breakseal techniques used in this investigation. Specific reaction details only will therefore be given here.

Synthesis of polymer derivatives of aluminium

Polyisoprene. t-Butyl lithium was used to initiate isoprene polymerization in hexane. Narrow dispersity polymers of low degree of polymerization were obtained with no detectable residual initiator. The conditions of oligomerization and the general experimental procedure have been described elsewhere[19,20]. The oligo polyisoprenyl lithium solutions were distributed quantitatively into vessels fitted with breakseals and sealed therein.

The reaction of the living oligomer with aluminium chloride was carried out in a 100 ml flask to which the ampoule containing living polyisoprene solution was fitted. $AlCl_3$ was added in a breakable glass bulb either as a solid or as a solution in cyclohexane. The reaction was complete in several hours in solution, but could take several days with solid $AlCl_3$. The mono-, di- and tri-alkyl substituted aluminium derivatives were prepared in this way by choosing the appropriate reagent stoichiometry.

The aluminium derivatives were characterized by elemental analysis and the disappearance of the absorption maximum at 270 nm observed with polyisoprenyl lithium. The totally alkylated compound was also analysed by ^1H n.m.r. By comparison with the spectrum of polyisoprenyl lithium[20] a new doublet was observed at 1.45 ppm corresponding to the methylene group adjacent to aluminium. This shift to lower field corresponds to a decrease in the ionic character of the methylene-aluminium bond compared with that involving lithium.

Polystyrene. n-Butyl lithium was employed to polymerize styrene in benzene. With this initiator, the rate of initiation is slower than that of propagation so that the consumption of catalyst is inefficient at low degrees of polymerization. The relationship[15] $[M] = 0.84\, k_p[C]^{4/3}/k_i$ was used to determine the minimum ratio of monomer to initiator required for complete consumption of initiator.

The reactions between the living polystyrene and $AlCl_3$ were carried out as described for polyisoprenyl lithium, and the aluminium derivatives obtained were characterized by elemental analysis and by the disappearance of the absorption maximum at 325 nm characteristic of polystyryl lithium.

Polymerization of ethylene

Ziegler-Natta polymerizations were carried out at −78°C under a constant pressure of 660 mm Hg with rapid stirring. $TiCl_4$ or $\alpha-TiCl_3$ was added to a benzene solution of the aluminium or lithium derivatives. The rate of consumption of ethylene was measured at constant pressure as described in an earlier publication[21]. The efficiency (e) of the polymerization process (see text) was determined after polymerization times ranging from 1 to 4 h.

Results and Discussion

The metal–alkyl cocatalyst is prepared by the initial polymerization of the appropriate monomer with a lithium alkyl initiator and, to produce the aluminium derivative, this is then reacted with aluminium halide at the appropriate molar stoichiometry. This synthesis is discussed initially, and subsequently the products of the interactions between these metal alkyls and titanium III and IV halides are examined as initiators of ethylene polymerization to form block copolymers.

Synthesis of polymer derivatives of aluminium. To prepare such aluminium derivatives uniquely by the reaction of living polymer with aluminium chloride, it is necessary that the living polymer be prepared under conditions which result in the total consumption of initiator. t-Butyl lithium was used to initiate isoprene polymerization in hydrocarbon solvent and, since the rate of initiation is much greater than that of propagation[14], narrow dispersity polymers of low degree of polymerization (down to $DP \sim 2.5$) were obtained with no detectable residual initiator.

n-Butyl lithium was employed to polymerize styrene in hydrocarbon media and, with this initiator, the rate of initiation is slower than that of propagation, so that the consumption of catalyst is inefficient at low *DP*s, indeed, calculation shows that *DP*s of about 100 are required in order to achieve close to quantitative initiation. Use of this catalyst imposed a limitation with polystyrene on the variation in ligand size which could be obtained on the aluminium alkyls. Clearly, for shorter chain derivatives more akin to those obtained with isoprene, a branched butyl lithium initiator should be used and such work is to be carried out. Nevertheless, the results obtained with the high *DP* materials are of interest and are reported here.

From the times at different reagent stoichiometries for the reaction between living polymer and aluminium chloride to go to completion, it is evident that alkylation of the aluminium becomes successively more difficult and slow. This means that addition of a given integral molar ratio of living polymer to $AlCl_3$ solution should generate the species with a degree of substitution corresponding to that ratio, rather than a distribution of products. This approach was therefore used to prepare the partially substituted species R_xAlCl_{3-x}.

Polymerization of ethylene. ZN polymerizations were carried out at $-78°C$ under a constant ethylene pressure of 660 mm Hg and with rapid stirring; conditions under which the rate of dissolution of monomer was sufficient to maintain its concentration in the reaction medium. The titanium salt employed with the aluminium or lithium derivatives was α-$TiCl_3$ or $TiCl_4$, and the following reaction parameters were examined: (a) the influence of the nature of the catalyst on the polymerizing efficiency of the system; (b) the effect of changing the molar ratio, r, of the aluminium or lithium derivative to titanium salt; (c) the effect of chain length of the ligand on catalytic activity, and (d) the temperature–reaction rate relationships of these catalytic systems.

The efficiency, e, of the reaction is determined by applying the formula $e=(M_T-M_E)/M_T$, where M_T = total weight of monomer and initiator used in the anionic polymerization, and M_E = weight of polymer, after copolymerization with ethylene, which is soluble in benzene or toluene. The soluble material is assumed to be unreacted homopolymer derived from the catalyst system and, indeed, ^1H n.m.r. examination of this product shows the absence of any absorption corresponding to polyethyelene — the spectra being identical to those of polyisoprene or polystyrene. These chains are assumed to result from unreacted alkyl ligands and from alkyl ligands involved in any reduction process. The unextracted polymer ligands are presumed to be bonded to the polyethylene chains to form block copolymers.

Typical results of such studies have been tabulated in *Table 1 a* and *b* for the polyisoprene ligand, and *Table 2 a* and *b* for the polystyrene ligand. In the case of isoprene and $TiCl_3$, the catalyst efficiency increases with r (*Table 1a*), and at all ratios the co-catalysts can be placed in the following order of efficiency: $AlR_3 > LiR > AlR_2Cl \gg AlRCl_2$. Similar results were obtained with $TiCl_4$, although the $AlRCl_2$ system was not examined with this salt. The effect of increasing the *DP* is to decrease the efficiency of the catalyst complex formed with either titanium compound (*Table 1b*), although the effect is not dramatic—a 30% loss being observed with a 150 fold increase in ligand chain length. Experiments carried out in the temperature range -78 to $+20°C$ (not tabulated) indicate that the efficiency at $r=1$ increased smoothly with temperature by $\sim 35\%$ over this interval.

With polystyrene ligands, only examined with α-$TiCl_3$, the situation is somewhat different; although the catalyst efficiency increases with r as with polyisoprene (*Table 2a*), the order of efficiencies is changed such that $LiR > AlR_2Cl > AlR_3$, i.e. AlR_3, the most effective cocatalyst when R is polyisoprene, is very inefficient when the ligand is polystyrene. The chain length of the ligand again has an adverse effect on the catalyst efficiency (*Table 2b*), the change being greater with polystyrene than with polyisoprene.

The similarity of the efficiencies obtained with polyisoprene derived catalysts from Ti IV and Ti III is perhaps surprising since in the former case a fraction of the aluminium or lithium alkyl is consumed in the reduction reaction (equations 1 and 2). The effect of total reduction of Ti IV to Ti III would be to reduce r from 3 to 2 (assuming the chlorinated reaction product to be catalytically inactive), so that the efficiency of the α-$TiCl_3$ system at $r=2$ should be compared with that of the $TiCl_4$ system at $r=3$. With isoprenyl lithium the efficiencies are very close, but with the aluminium derivatives the $TiCl_4$ efficiency is higher. Perhaps this is linked with the fact that the chlorinated aluminium product from the reduction is also catalytically active. The process of catalyst formation is, however, complex and a direct correlation with the simplified mechanism outlined above is, perhaps, optimistic to expect.

The catalytic efficiency of the polyisoprene based systems is only marginally affected by *DP* up to a value of about 10, and is smoothly but slowly reduced thereafter. The work of Siove and Fontanille[13] predicts a transition from heterogenous to homogenous catalyst over this range, but this is not reflected in any abrupt change in the initiating efficiency of the catalyst systems examined. The observed gradual reduction of efficiency with increased *DP* may be interpreted merely as a reducing accessibility

Table 1a Efficiency of catalyst systems involving polyisoprene: polyisoprene of *DP* ~3

	α-Ti Cl_3			Ti Cl_4		
Catalyst ratio (*r*)	3	2	1	3	2	1
Al R_3	0.33	0.26	0.22	0.35	0.31	0.27
Al R_2Cl	0.17	0.10	0.08	0.25	0.23	0.19
Al RCl_2	0.02	0.01	0.01	–	–	–
Li R	0.26	0.22	0.17	0.24	0.21	0.20

Table 1b Effect of degree of polymerization

	α-Ti Cl_3 (at *r* = 1)							Ti Cl_4 (*r* = 3)					
DP	3	10	50	100	150	300	450	3	10	50	150	300	450
Al R_3	0.22	0.24	0.18	0.18	0.15	0.17	0.15	0.35	0.35	0.31	0.28	0.28	0.25
Li R	0.17	0.15	0.14	–	0.14	–	0.12	0.24	0.25	0.23	0.20	–	0.19

Table 2a Efficiency of catalyst systems involving polystyrene: polystyrene (*DP* ~100) and α-Ti Cl_3

Catalyst ratio (*r*)	3	2	1
Al R_3	0.04	0.03	–
Al R_2 Cl	0.16	0.10	0.06
Li R	0.18	0.12	0.05

Table 2b Effect of degree of polymerization at *r* = 3

DP	100	200	300
Li R	0.18	0.12	0.03

of the ethylene monomer to the catalytic site.

A similar explanation may be advanced for the relative catalytic activities of the initiators derived from polystyrene (*Table 2b*) in which an inverse relationship was found between the activity and the degree of substitution of the metal alkyl component. The greater bulk of polystyrene chains makes steric factors more important, such that the least bulky component, LiR, has the greatest activity, whereas the most bulky, AlR_3, is very much less.

If the assumption be accepted that the non-extractable homopolystyrene or polyisoprene from the products of these polymerizing systems is due to block copolymer formation, then these experiments demonstrate the feasibility of preparing such copolymers by this means. There remains a possibility, however, that the unextractable homopolymer is physically entrapped within the polyethylene matrix rather than chemically bound thereto. The following observations, nevertheless, make the latter explanation unlikely: (a) the homopolymer is soxhlet extracted rapidly by benzene, but after about 24 h no further material is solubilized, (b) the fraction of extractable material is reproducible in repeat experiments, (c) the catalyst efficiency increases with r, which means that the fraction of extractable polymer *decreases* as the proportion of the polymer derivative added *increases*.

Absolute confirmation of block copolymer formation can best be obtained by high temperature g.p.c., a technique to which we currently have no access. Nevertheless, these materials will be examined in this way in the future, when a fuller report will be made on the kinetics of the process and characterization of the products.

Lastly, it should be noted that the efficiencies quoted refer exclusively to the conversion of the polymer ligands into block copolymers. No assessment has been made of the molar per cent of block copolymer in the product. This could be 100% in the solvent extracted material if no chain transfer reactions took place during ZN polymerization, down to a low figure if such reactions were prevalent.

References

1 Burgess, F. J., Cunliffe, A. V., Richards, D. H. and Sherrington, D. C. *J. Polym. Sci., Polym. Lett. Edn.* 1976, **14**, 47

2 Burgess, F. J., Cunliffe, A. V., McCallum, J. R. and Richards, D. H. *Polymer* 1977, **18**, 719

3 Burgess, F. J. and Cunliffe, A. V., McCallum, J. R. and Richards, D. H. *Polymer* 1977, **18**, 726

4 Burgess, F. J., Cunliffe, A. V., Dawkins, J. V. and Richards, D. H. *Polymer* 1977, **18**, 733

5 Abadie, M. J. M., Burgess, F. J., Cunliffe, A. V. and Richards, D. H. *J. Polym. Sci., Polym. Lett. Edn.* 1976, **14**, 477

6 Cunliffe, A. V., Hayes, G. F. and Richards, D. H. *J. Polym. Sci., Polym. Lett. Edn.* 1976, **14**, 483

7 Souel, T., Schué, F., Abadie, M. J. M. and Richards, D. H. *Polymer* 1977, **18**, 1292

8 Souel, T., Schué, F., Abadie, M. J. M. and Richards, D. H. *Polymer* 1981, **22**, 1076

9 Cohen, P., Schué, F., Abadie, M. J. M. and Richards, D. H. *Polymer* 1981, in press

10 Richards, D. H. *Brit. Polym. J.* 1980, **12**, 89

11 Ziegler, K., Holzkamp, E., Breil, H. and Martin, H. *Angew. Chem.* 1955, **67**, 541

12 Natta, G. *J. Polym. Sci.* 1955, **16**, 143

13 Siove, A. and Fontanille, M. *Makromol. Chem.* 1980, **181**, 1815

14 Bywater, S. and Worsfold, D. J. *Adv. Chem. Sci.* 1966, **52**, 56

15 Worsfold, D. J. and Bywater, S. *Can. J. Chem.* 1960, **38**, 1891

16 Bywater, S. and Worsfold, D. J. *J. Phys. Chem.* 1966, **70**, 152

17 Worsfold, D. J. and Bywater, S. *Can. J. Chem.* 1964, **42**, 2884

18 Roovers, J. E. L. and Bywater, S. *Macromolecules* 1968, **1**, 328

19 Schué, F., Worsfold, D. F. and Bywater, S. *J. Polym. Sci. B* 1969, **7**, 821

20 Bywater, S., Schué, F. and Worsfold, D. J. *Macromolecules* 1970, **3**, 509

21 Rodriguez, F., Abadie, M. J. M. and Schué, F. *J. Polym. Sci., Polym. Chem. Edn.* 1976, **14**, 773

Stereospecific polymerization of *N*-vinylcarbazole by $ZnEt_2/CoCl_2$–pyridine catalyst system

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Introduction

Little established work on the stereospecific polymerization of N-vinylcarbazole at ambient temperature has been reported. Some of the work reported[1] is irreproducible and has been contradicted[2]. In the course of our work on the development of sterospecific catalyst systems based on oxychloride–metal alkyl combinations[3,4], we have observed that cobalt chloride pyridine complex is particularly effective in presence of zinc diethyl in producing stereoregular poly(*N*-vinylcarbazole) at room temperature. A cobalt chloride–pyridine–$AlEt_2Cl$ catalyst system has been used for the *cis*-polymerization of butadiene and isoprene[5]. Interestingly, the molecular weights of poly(*N*-vinylcarbazole) produced under these conditions are much higher than those reported by us for the aprotonic acids[6,7], Grignard reagent[8,9] and the metal oxide[10,11] initiated polymerization of this monomer. This communication highlights some relevant observations on this system.

Experimental

Monomers. *N*-vinylcarbazole (NVC), (BASF — West Germany), styrene (S) ICI. Plastics Division and iso-butyl vinylether (IBVE) E. Merck were purified, distilled and preserved following standard techniques[6,12,13].

Preparation of the catalyst. The hydrocarbon soluble cobalt chloride pyridine complex was prepared by adding a calculated amount of pyridine to a known quantity of anhydrous cobalt chloride[14] in a pyrex test-tube under nitrogen atmosphere. The deep blue complex formed was freely soluble in toluene and was stable for a considerable period (one month). Solutions of desired concentration were prepared conventionally. All dilutions and handling

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