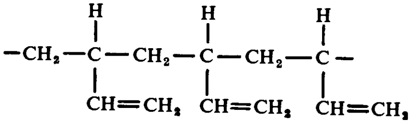
The Polymerization and Copolymerization of Butadiene

By D. H. Richards
EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT,
MINISTRY OF DEFENCE, WALTHAM ABBEY, ESSEX EN9 1BP

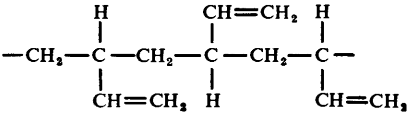
1 Introduction

The polymerization of butadiene, whether uniquely to form homopolymers or with other monomers to form copolymers, is a process of great industrial importance. Production of butadiene-containing elastomers in the Western World in 1975 exceeded 3.6 million tons, and constituted about 50% of all rubber and 70% of all synthetic rubber consumed.

The properties of polybutadiene (PBD) depend on the way in which the monomer is incorporated into the chain. Butadiene can be polymerized by either 1,2- or 1,4-addition. If polymerization takes place to give the 1,2- or vinyl form exclusively, then two types of stereoregular sequences can arise; one in which the asymmetric carbon atoms have the same configuration [isotactic placement, (1)] or one in which the configuration alternates [syndiotactic placement, (2)]. Stereospecific polymerization in the 1,4-mode produces a *cis*-PBD (3) or a *trans*-PBD (4). The four distinct stereoregular homopolymers have been prepared



(1)



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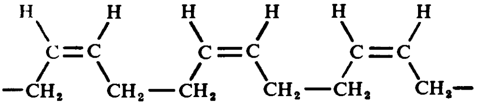

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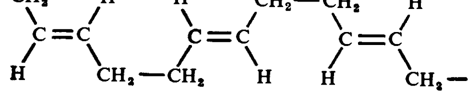

(4)

and shown to have very different properties. The isotactic and syndiotactic PBD's are rigid, crystalline and virtually insoluble materials, whereas *cis*-PBD is a soft, readily soluble elastomer with a glass transition temperature (*Tg*)* around -100 °C. It has a high retractive force and crystallizes at extensions greater than 200% (*cf.* the isoprene analogue, hevea rubber). In contrast, *trans*-PBD is hard, difficultly soluble and crystallizes without elongation (*cf.* the isoprene analogue, gutta percha).

PBD's of mixed structure (atactic PBD's) may be conveniently regarded as copolymers with different isomers being taken as individual component monomers. In this way the distribution of components along the chain can more easily be considered, and PBD's may be envisaged with structures ranging from alternating copolymers to block copolymers. Indeed the 'blockiness' of PBD's produced by various catalyst systems is currently a subject of considerable debate.

The best elastomeric properties are exhibited by high *cis*-PBD and, initially, methods of preparing this material were sought. It was later found that the sole important structural requirement for a good cross-linked or vulcanized rubber was that it should have a low vinyl content. *cis–trans* Isomerization occurs under vulcanization conditions,[1] and the final properties of the product after correct compounding and vulcanization are insensitive to the initial *cis–trans* ratio.

2 Structural Analysis

Present day methods of determining the structures of PBD's are entirely based on spectroscopic techniques. The earliest and most used of these is infra-red (i.r.) spectroscopy, but nuclear magnetic resonance (n.m.r.) spectroscopy can now give a more accurate estimate of the molecular architecture of those polymers with low vinyl content.

A. IR Spectroscopy.—The *trans* and vinyl content of PBD's may be readily determined from the bands at 970 cm^{-1} and 910 cm^{-1} respectively. The *cis* component, however, absorbs over a broad band near 715 cm^{-1} which varies unpredictably in wavelength with the sample and can overlap other peaks. This problem has been critically reviewed[2] and a method has been recommended which involves integrating the absorbance between 830 cm^{-1} and 635 cm.^{-1} A simpler method was later proposed[3] which is satisfactory in most cases.

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*Tg is an important characteristic of a polymer system. Although not thermodynamic in origin, it indicates the onset of segmental motion of polymer chains and marks the temperature above which the physical properties of a material transform from those characteristic of glass to those of rubber.

[1] J. I. Cunneen, G. M. C. Higgins, and W. F. Watson, *J. Polymer Sci.*, 1959, **41**, 1.

[2] R. S. Silas, J. Yates, and V. Thornton, *Analyt. Chem.*, 1959, **31**, 529.

[3] J. Haslam, H. A. Willis, and D. C. M. Squirrell, 'Identification and Analysis of Plastics', Iliffe Books, 1972.

B. Raman Spectroscopy.—Cornell and Koenig[4] have shown that the Raman double bond stretching vibrations can be used to describe PBD's. All three C=C vibrations are Raman active, and the stretching frequencies have been determined as 1650 cm^{-1} (*cis*), 1664 cm^{-1} (*trans*), 1655 cm^{-1} (vinyl) and 1639 cm^{-1} (isolated vinyl). Since the vibrations are all in the same spectral region, the authors assume the extinction coefficients to be in a constant ratio to each other, and they determine the structural composition from the peak areas.

C. NMR Spectroscopy.—The proportions of the three isomers may be determined by ^{1}H n.m.r. spectroscopy, and both this technique and ^{13}C n.m.r. spectroscopy may be employed to determine the isomer distribution along the chain. The success of the latter analysis relies upon the identification of resonances as being due to specific structural sequences. For example, in a *cis–trans* (*c–t*) PBD in which resonances are observed at frequencies characteristic of a triad structure, the intensities of the *tcc*, *tct*, *ctt* and *ctc* bands relative to the *ccc* and *ttt* bands should give a direct measure of the 'blockiness' of the sample. These resonances must therefore be accurately assigned and, unfortunately, controversy still exists in this area.

Early low field ^{1}H n.m.r. studies were able to determine the relative proportions of vinyl and 1,4-linkages in PBD but could not distinguish between the *cis* and *trans* configurations[5] (Table 1, column 3). More recently, Morton and co-workers[6] working at 300 MHz and Hatada *et al.*[7] working at 100 MHz showed that an analysis of *cis* and *trans* structure could be obtained in high 1,4-PBD's. At 300 MHz both the olefinic and aliphatic resonances consist of a pair of broad peaks (Table 1, column 4) and, when the aliphatic peaks were irradiated, the olefinic resonances were each resolved into three peaks corresponding to triads of *cis* and *trans* units. However, when the olefinic peaks were irradiated, one group found no change in the aliphatic resonance,[6] whilst the other obtained a triplet centred at 2.06 δ[7] which was assigned to the three possible doublets (Table 1, column 5). This discrepancy may, however, be more apparent than real since the measurements were carried out in different solvents and at different temperatures.

As the proportion of vinyl units increases, interference occurs in the olefinic region and it is recommended that the *cis–trans* content be determined in the aliphatic region. Even here analysis becomes difficult at more than 60% vinyl structure because of overlap with the methine proton of the vinyl group.

The ^{13}C n.m.r. spectra of PBD's containing all possible linkages are extremely

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[4] S. W. Cornell and J. L. Koenig, *Rubber Chem. Technol.*, 1970, **43**, 322.

[5] H. Y. Chen, *Analyt. Chem.*, 1962, **34**, 1134, 1793.

[6] E. R. Santee, jun., L. O. Malotsky, and M. Morton, *Rubber Chem. Technol.*, 1973, **46**, 1156; E. R. Santee, jun., R. Chang, and M. Morton, *J. Polymer Sci. B*, 1973, **11**, 449; E. R. Santee, jun., V. D. Hochel, and M. Morton, *J. Polymer Sci. B*, 1973, **11**, 453.

[7] K. Hatada, Y. Tanaka, Y. Terawaki, and H. Okuda, *Polymer J. Japan*, 1973, **5**, 327; K. Hatada, Y. Terawaki, H. Okuda, Y. Tanaka, and H. Sato, *J. Polymer Sci. B*, 1974, **12**, 305.

Table 1 ^{1}H *N.m.r. absorptions of polybutadiene*

Structure	*Hydrogen Location*	*Low Field*	*High Field*	*High Field Spin Decoupled*
$1,4\text{—}\underset{\beta}{CH_2}\text{—}\underset{\alpha}{CH}=CH\text{—}CH_2\text{—}$	α	5.3^a	5.32 (*cis*)^b 5.37 (*trans*)^b	5.307 (*tct*)^b 5.315 (*cct*)^b 5.324 (*ccc*)^b 5.356 (*ttt*)^b 5.365 (*ctt*)^b 5.375 (*ctc*)^b
	β	2.0^a	1.98 (*cis*)^b 2.03 (*trans*)^b	3.04 (*tt*)^c 2.06 (*ct*)^c 2.09 (*cc*)^c
$1,2\text{—}\overset{\delta}{CH_2}\text{—}\overset{\gamma}{CH}\text{—}$ $\qquad\quad \vert$ $\qquad \underset{\alpha}{CH}=\underset{\beta}{CH_2}$	α	5.3^a		
	β	5.0^a		
	γ	2.0^a		
	δ	1.3^a		

^{a} = deuterochloroform solvent, tetramethylsiloxane reference, T = ambient, from ref. 5. ^{b} = *o*–dichlorobenzene solvent, hexamethyldisiloxane reference, T = 110 °C, from ref. 6. ^{c} = deuterochloroform solvent, tetramethylsiloxane reference, T = 35 °C, 45 °C, from ref. 7.

complicated and it is necessary to consider the various stereospecific types separately. The spectra of 1,4-PBD's reveal relatively little detailed information even at 67.88 MHz; the aliphatic carbons give two well separated peaks at about 28 and 33 p.p.m. relative to tetramethylsilane (TMS) due to *cis* and *trans* linkages respectively,[8] and even at high fields show no further splitting due to sequence distribution.[9] Only slightly more information is obtained from the olefinic region; four peaks are observed at 130.10, 130.25, 130.75 and 130.85 p.p.m. relative to TMS[8] which are assigned to *tc**, *cc**, *tt** and *ct** diad resonances (the asterisk denotes the unit containing the observed carbon).

Elgert *et al.*, examining vinyl PBD's at 67.88 MHz,[10a] interpreted the olefinic methylene peak at 113.4 p.p.m. and the methine peak at 142.5 p.p.m. in terms of pentad sequences arising from the different stereochemical arrangements of the vinyl units. They subsequently studied *cis*-vinyl PBD[10b] and found these absorbances complicated by 1,2-configurational and compositional 1,2–1,4 sequence effects, but the *cis* region at about 129 p.p.m. was intepreted in terms of 1,2–1,4 triad sequences. Similar interpretations have been given by other authors,[11]

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[8] F. Conti, A. Segrè, P. Pini, and L. Porri, *Polymer*, 1974, **15**, 5.

[9] K. F. Elgert, B. Stützel, P. Frenzel, H-J. Cantow, and R. Streck, *Makromol. Chem.*, 1973, **170**, 357.

[10] (*a*) K. F. Elgert, G. Quack, and B. Stützel, *Makromol. Chem.*, 1974, **175**, 1955; (*b*) *idem.*, *Polymer* 1974, **15**, 613.

[11] J. Furukawa, E. Kobayashi, N. Katsuki, and T. Kawagoe, *Makromol. Chem.*, 1974, **175**, 237.

although Conti *et al.*,[12a] analysing the aliphatic absorbances of equibinary *cis*-vinyl, 15% *cis*-85% vinyl, and 6% *trans*-94% vinyl PBD's gave some assignments which differ.

Elgert *et al.*[12b] also analysed mixed structured PBD's prepared anionically and assigned the 1,4-olefinic carbon resonances in terms of triad sequences. A similar interpretation was made by Clague *et al.*[13] who also demonstrated that further useful information could be obtained from hydrogenated material, as this simplified the spectrum.

3 Emulsion Polymerization

Butadiene is not easily polymerized to high molecular weights by conventional free-radical initiators in solution or in bulk, although the polymeric material has the desired high 1–4 structure ($\sim 80\%$). The products are mixtures of a low molecular weight soluble fraction (sol) and a cross-linked gel, the proportions of which depend on the reaction conditions. This behaviour is caused by a low velocity of propagation ($\sim 8\ \mathrm{l\ mol^{-1}\ s^{-1}}$)[14] competing with a very fast termination step ($\sim 10^8\ \mathrm{l\ mol^{-1}\ s^{-1}}$)[15] and a rapid cross-linking reaction ($\sim 8 \times 10^{-2}\ \mathrm{l\ mol^{-1}\ s^{-1}}$),[16] and results in an excessive degree of branching under high conversion conditions. For these reasons, the homogeneous free radical polymerization of butadiene is now used commercially, principally to prepare low molecular weight (<5000) functionally terminated liquid polymers; even in these systems the conversion is kept very low ($\sim 40\%$) and with only a minimal amount of solvent added.

The slow growth rates and short lifetimes of butadienyl radicals mean that the rate of termination must be reduced to obtain a high molecular weight product, and this is best effected by confining the propagating radicals in the micelles of an emulsion. These emulsion processes are of great industrial importance, particularly for the copolymerization of butadiene with styrene or with acrylonitrile to form styrene–butadiene rubber (SBR) or nitrile rubber. An excellent review of the subject has appeared recently,[17] and the salient features of the process as applied to butadiene will be outlined here.

An aqueous dispersion of the monomer is made using an emulsifying agent or soap, which consists of droplets of about 1 μm in diameter stabilized by a monolayer of soap, and soap micelles of about 75 Å diameter which contain occluded monomer. The monomer is primarily stored in the droplets, but is in

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[12] (*a*) F. Conti, M. Delfini, A. L. Segrè, D. Pini, and L. Porri, *Polymer*, 1974, **15**, 816; (*b*) K. F. Elgert, G. Quack, and B. Stützel, *Polymer*, 1975, **16**, 154.

[13] A. D. H. Clague, J. A. M. von Broekhaven, and L. P. Blaauw, *Macromolecules*, 1974, **7**, 348.

[14] M. Morton, P. P. Salatiello, and H. Landfield, *J. Polymer Sci.*, 1952, **8**, 215.

[15] W. Cooper and G. Vaughan, 'Progress in Polymer Science', ed. A. D. Jenkins, Vol. 1, Pergamon Press, 1967, 93.

[16] R. A. Hayes, *J. Polymer Sci.*, 1954, **13**, 583.

[17] D. C. Blackley, 'Emulsion Polymerisation', Applied Science, London, 1975.

equilibrium with that located in the micelles *via* the small amount in true solution. Addition of a water soluble radical initiator, usually a persulphate or a redox system, allows radicals to be generated in the aqueous phase which migrate to the soap micelles wherein they initiate polymerization. The radicals are predominantly absorbed by the micelles rather than the droplets because of the very much greater surface area they present as a result of their large number ($\sim 10^{14}$ cm^{-3}) and small size.

Propagation continues, fed by the monomer from the droplets so that they decrease in size as the micelles swell to form monomer–polymer particles. The growth of these particles increases the surface area to a point at which all the free emulsifier is adsorbed, and hence no new particles are formed–end of Stage I of this process. This point is usually reached rather early in the reaction (about 10—15% conversion at normal soap loadings), and thereafter the constant particle concentration results in a constant rate of polymerization until the monomer droplet phase is consumed–end of Stage II. This occurs at about 52% conversion with butadiene at 50 °C using a standard persulphate recipe.[18] The third and final stage involves the polymerization of the residual monomer in the monomer–polymer particles, but emulsion polymerizations involving dienes are normally halted at about 60—70% conversion in order to avoid excessive branching and cross-linking. Therefore the bulk of the polymer is formed under the steady-state conditions prevailing under Stage II.

After Harkins[19] had demonstrated that polymerization was initiated in the micelles and that propagation continued at these sites after their transformation into particles, Smith and Ewart[20] developed an elegantly simple equation to express the kinetics of the process. The theory required the conditions that (i) the monomer was only slightly soluble in water, (ii) the polymer was soluble in monomer, and (iii) the radicals were generated in the aqueous phase. If the assumption were then made that the termination of a radical in a particle took place very rapidly on the introduction of another compared with the interval between the entrance of successive radicals, then at any given time one half of the particles would contain a single radical and the other half would contain none. Therefore, under the steady-state conditions applying at Stage II, the rate of polymerization is given by equation (1), where k_p is the rate constant of propagation in bulk, [M] is the monomer concentration in the particle, and N is the number of particles. In typical emulsion systems the particle concentration is approximately 10^{14} cm^{-3} and the rate of radical generation is about 10^{13} cm^{-3} s^{-1}, so that propagating radicals have lifetimes of the order of 10 s. Under these conditions polybutadienyl radicals can grow to high molecular weight despite

$$-d[\mathrm{M}]/dt = k_p[\mathrm{M}]N/2 \qquad (1)$$

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[18] E. J. Meehan, *J. Amer. Chem. Soc.*, 1949, **71**, 628.

[19] W. D. Harkins, *J. Amer. Chem. Soc.*, 1947, **69**, 1427; *J. Polymer Sci.*, 1950, **5**, 217.

[20] W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, 1948, **16**, 592.

their slow propagation rate. Critical reviews of the theories relating to emulsion polymerization have been recently published.[21,22]

Polymerizations involving butadiene almost exclusively use anionic emulsifiers such as the alkali metal salts of fatty acids between C_{12} and C_{18} used either alone or in conjunction with rosin acid soaps. They are effective between pH 9 and 11, and may be coagulated in acid media. Emulsifier concentrations are of the order of 5 parts per 100 monomer. An electrolyte, typically KCl, is often dissolved in the aqueous phase where it can reduce the critical micelle concentration and, by increasing the particle size through partial agglomeration, lower the viscosity of the final latex.

The Smith–Ewart theory predicts that at Stage II the relationship indicated in equation (2) should hold (E and I are the emulsifier and initiator concentrations),

$$-d\mathrm{M}/dt \propto [E]^{0.6}[I]^{0.4} \tag{2}$$

and results from SBR polymerizations indicated the emulsifier and initiator exponents to be 0.7 and 0.4—0.5 respectively,[23] in reasonable agreement with theory. This relationship shows that if insufficient emulsifier is present the number of propagating particles is small, so that they grow too large and agglomeration and flocculation results.

The initiators used in butadiene polymerization fall into two categories, persulphate–mercaptan combinations and redox systems. Potassium persulphate alone initiates many monomer systems; thermal decomposition at about 50 °C produces two sulphate radical ions [equation (3)]. These radicals, however,

$$S_2O_8^{2-} \rightarrow 2\cdot SO_4^{-} \tag{3}$$

initiate butadiene only inefficiently in the absence of a mercaptan, and Duck[24] has argued that the radical anion is highly polar and cannot readily penetrate into the non-polar latex particle. He postulates that the use of a mercaptan promoter, typically a C_{12} molecule, allows the less polar mercaptyl radicals to be formed by reaction (4) which can enter the particles more easily. Care has to be

$$\cdot SO_4^{-} + RSH \rightarrow HSO_4^{-} + RS\cdot \tag{4}$$

taken with the use of mercaptans, however, as they are also molecular weight modifiers (see later).

SBR and nitrile rubbers prepared at 55 °C using the persulphate catalyst system are known as hot polymerized rubbers. The later development of redox initiators allowed the polymerization temperature to be lowered, typically to

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[21] A. E. Alexander and D. H. Napper, 'Progress in Polymer Science', ed. A. D. Jenkins, Vol. 3, Pergamon Press, 1971, 145.

[22] J. Ugelstad and F. K. Hansen, *Rubber Chem. Technol.*, 1976, **49**, 536.

[23] I. M. Kolthoff and A. I. Medalia, *J. Polymer Sci.*, 1950, **5**, 391.

[24] E. W. Duck, J. A. Waterman, and G. E. Latteij, *J. Appl. Chem.*, 1962, **12**, 469.

5 °C, and the rubbers resulting, known as cold polymerized rubbers, had generally superior physical and mechanical properties. The most satisfactory type of redox initiator for butadiene consists of a monomer soluble hydroperoxide (*p*-menthane, pinane or cumene) and a water soluble reducing system. The latter component consists of a ferrous salt complexed with a pyrophosphate or EDTA, and a reducing agent such as glucose or a sulphoxylate. Alkoxide radicals are generated by reduction of the hydroperoxide by free ferrous ions, equation (5),

$$\mathrm{ROOH} + \mathrm{Fe}^{2+} \rightarrow \mathrm{RO}\cdot + \mathrm{OH}^- + \mathrm{Fe}^{3+} \qquad (5)$$

and the resulting ferric species are converted back to the ferrous state by the reducing agent. Ferric ions can react directly with hydroperoxide to produce peroxy radicals (ROO·) but these are incapable of initiating polymerization. For this reason, air is kept out of emulsion systems as oxygen inhibits polymerization by converting the alkoxy radical into the inactive peroxy radical. Oxygen scavengers such as sodium dithionate are also often added.

The molecular weights of emulsion polymers are controlled by the addition of chain transfer agents, otherwise known as modifiers. Mercaptans have most frequently been employed in this role [equation (6)] and their efficiencies have

$$\mathrm{RSH} + \mathrm{M}_n\cdot \rightarrow \mathrm{M}_n\mathrm{H} + \mathrm{RS}\cdot \qquad (6)$$

been shown to be governed by two factors (i) their rates of diffusion from the monomer droplets to the growing particles, and (ii) their rates of chain transfer with propagating radicals. The C_{12} mercaptans give the optimum performances in this regard and are now generally used. A detailed review of the molecular weight control of emulsion polymers has recently been published.[25]

Butadiene based emulsion systems are prone to cross-linking and gelling, and polymerization must be terminated at about 65% conversion to minimize this effect. Compounds used in this role are called short stops, and they deactivate the reagents in the aqueous phase and terminate the growing radicals in the particles. Examples of such compounds are hydroquinone, sodium polysulphide, and phenylhydrazine.

It has been shown that the microstructure of the butadiene component of a polymer is little affected by changes in initiator, soap or modifier.[26] Changing the polymerization temperature principally affects the *cis–trans* ratio, the vinyl content remaining at about 18%; at 5 °C the *trans* content is 70% and drops to 63% at 50 °C.[26]

The butadiene component in nitrile rubbers possesses a higher *trans* content than the homopolymer or SBR; thus nitrile rubber prepared at 28 °C and containing 28% acrylonitrile has the butadiene structure 12% *cis*, 78% *trans* and 10% vinyl. Both the cold SBR and the cold nitrile rubbers have narrower molecular weight distributions than the hot variety, and this is attributable to the activation

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[25] C. A Uraneck, *Rubber Chem. Technol.*, 1976, **49**, 536.

[26] J. L. Binder, *Ind. and Eng. Chem.*, 1954, **26**, 1727.

energy of transfer (70 kJ mol^{-1}) being considerably larger than that of propagation (39 kJ mol^{-1}).

The emulsion technique as applied to butadiene is used chiefly to produce SBR and nitrile rubbers, and in these circumstances the copolymerization equation [equation (7)] applies, where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. The monomer

$$\frac{dM_1}{dM_2} = \frac{[M_1]}{[M_2]}\left(\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}\right) \tag{7}$$

concentrations refer to those in the particles, which may be different from those in the storage oil droplets. However, Lewis *et al.*,[27] measuring the reactivity ratios (r) of bulk styrene (M_1)–butadiene (M_2) systems at 60 °C obtained $r_1 = 0.78$ and $r_2 = 1.39$, close to those obtained in emulsion systems at 50 °C[28] ($r_1 = 0.64$, $r_2 = 1.38$) so that the differences in monomer concentration are probably not large. The latter values give $r_1r_2 = 1.08$ which is near the unity required for ideal copolymerization.

This ideal situation arises when the relative reactivities of both monomers are the same toward either of the two possible growing ends, and implies that the relative molar concentration of monomers in the copolymer and in the emulsion mixture are the same at all monomer ratios. The consequent constancy of composition of product with conversion is quite closely obeyed by SBR, particularly at low polymerization temperatures.[28]

These copolymerization conditions do not apply for nitrile rubbers. Although, like SBR, the reactivity ratios obtained for acrylonitrile (M_1)–butadiene (M_2) systems in bulk and in emulsion agree well,[29] the absolute figures of $r_1 = 0.28$, $r_2 = 0.02$ at 5 °C and $r_1 = 0.42$, $r_2 = 0.04$ at 5 °C are very different, with $r_1r_2 \ll 1$. This relationship means that there is only one ratio of monomers at a given temperature where the polymer composition is constant with conversion. This so called azeotropic mixture is calculated from equation (8), and has a value of 36%

$$[M_1]/[M_2] = (r_2 - 1)/(r_1 - 1) \tag{8}$$

acrylonitrile at 5 °C and 42% acrylonitrile at 50 °C.

4 Anionic Polymerization

Although the polymerization of dienes by alkali metals was first revealed in 1910—11 by patents issued to Matthews and Strange[30] and to Harris,[31] the first systematic study of these and similar systems initiated by alkyl lithium was carried out by Ziegler and co-workers in the mid-thirties.[32] They distinguished between the initiation step and the subsequent propagation step and established

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[27] F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs, and W. Weiniseh, *J. Amer. Chem. Soc.*, 1948, **70**, 1527.

[28] R. D. Gilbert and H. L. Williams, *J. Amer. Chem. Soc.*, 1952, **74**, 4144.

[29] W. V. Smith, *J. Amer. Chem. Soc.*, 1948, **70**, 2177.

[30] F. E. Matthews and E. H. Strange, B.P. 24 790/1910.

[31] C. H. Harries. U.S.P. 1 058 056/1913; *Annalen*, 1911, **383**, 184.

[32] K. Ziegler, F. Dersch, and H. Wolltham, *Annalen*, 1934, **511**, 13, 45, 64.

that, whereas initiation with alkyl lithium produced a species which could propagate at one end [equation (9)], direct alkali metal initiation yielded a diadduct capable of propagation at both ends [equation (10)]. Although the

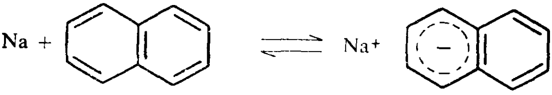
$$\text{RLi} + \text{M} \rightarrow \text{RMLi} \xrightarrow{n\text{M}} \text{RM}_{n+1}\text{Li} \qquad (9)$$

$$2\text{Li} + \text{M} \rightarrow \text{LiMLi} \xrightarrow{n\text{M}} \text{LiM}_{n+1}\text{Li} \qquad (10)$$

process was not described as anionic, the concept that these systems were ones which need not possess a termination step, now called 'living' systems, was quite clearly perceived.

Some general deductions may be made from Ziegler's scheme. Unlike free radical systems, in the absence of chain transfer processes or impurities the polymer molecular weight will increase with conversion. Furthermore, since in alkyl lithium initiation one polymer chain is generated for each initiator molecule consumed (C), the number average molecular weight (M_n) is given by $M_n = M/C$, where M = weight of monomer consumed. With initiation fast relative to propagation this relationship approximates to $M_n = M/C_0$, where C is the initial catalyst concentration. Similarly, for alkali metal initiation $M_n = 2M/C$ ($\approx 2M/C_0$ for fast initiation). Finally, the molecular weight distribution in both cases should be Poisson with fast initiation ($M_w/M_n \rightarrow 1$ at high molecular weights).

More recently, alkali metal adducts of polycyclic hydrocarbons, prepared by direct reaction of the components in polar solvents, were found to act as anionic initiators by an electron transfer mechanism.[33] Typically, sodium reacts with naphthalene in tetrahydrofuran (THF) to form the radical anion (5) in which the



(11)

(5)

electron occupies the lowest vacant π-orbital of the naphthalene. These species ($\text{Na}^+ \text{N}^{\overline{\cdot}}$) initiate by electron transfer to monomer, and the monomer radical anion thus formed dimerizes to give the dimer dianion which propagates further [equation (12)]. In one sense these catalysts may be regarded as solubilized forms

$$\text{Na}^+\text{N} + {}^{\overline{\cdot}}\text{M} \rightleftharpoons \text{N} + \text{Na}^+\text{M}^{\overline{\cdot}} \xrightarrow{\text{dim}} \text{Na}^+\text{M}_2^{2-}\ \text{Na}^+ \xrightarrow{(n-2\text{M})} \text{Na}^+\text{M}_n^{2-}\,\text{Na}^+ \qquad (12)$$

of alkali metal with the consequent advantage of very much faster rates of initiation. Unfortunately, however, they are stable only in good cation solvating solvents which, as will be seen, adversely affect PBD structure.

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[33] M. Szwarc, M. Levy, and R. Milkovich, *J. Amer. Chem. Soc.*, 1956, **78**, 2656.

A. Alkali-metal Initiation.—PBD prepared by alkali metal initiation has a structure determined by the nature of the metal rather than the presence or otherwise of inert hydrocarbon solvents. High 1,4-PBD (~90%) is produced with lithium, about 40% of which is *cis*.[34,35] These heterogeneous reactions are slow, with initiation and propagation proceeding simultaneously, so that broad molecular weight distributions result. Initiation by alkali metals other than lithium, or even their alloys with lithium, produces PBD's with greatly increased vinyl content (~60%).[34,35]

Introduction of a polar solvent such as THF accelerates the rate of reaction, but its presence has a dramatic effect on the PBD structure; all *cis* structure is eliminated and up to 90% vinyl conformation is formed. The same behaviour is observed with electron-transfer catalysts.[36]

It is therefore clear that the desired high 1,4-PBD's can only be prepared anionically using lithium as the counter ion, and in the absence of a polar solvent. These conditions may be realised by using alkyl lithium initiators and, as these systems are homogeneous and consequently more reproducible than those involving the metal, they have been the subject of much study.

B. Alkyl Lithium Polymerization.—All alkyl lithiums except the methyl derivative are soluble in hydrocarbon solvent in which they exist in associated forms; ethyl lithium and butyl lithium are hexameric whereas the branched and larger chain species exist as tetramers.[37] This aggregation complicates the analysis for the polymerization process because propagation results in polymeric lithium species which form mixed aggregates with residual lithium initiator.[38] Further, the inadvertent presence of other lithium compounds such as halides or alkoxides can influence the rate of initiation by participating in the aggregation.[39]

Kuntz and Greber,[40] using isobutyl lithium in heptane as initiator, showed that PBD possessed a structure unaffected by changes in initiator or monomer concentration or by degree of conversion; it was also relatively insensitive to polymerization temperature over a wide range. Similarly, the alkyl lithium initiator used does not affect the microstructure of the polymer, although it does have a marked effect on the kinetics and hence the molecular weight and dispersity of the product. Change of hydrocarbon solvent also principally alters the rate of polymerization rather than the molecular architecture of the polymer; catalysts in aromatic solvents initiate more rapidly than in aliphatic media, but PBD's from these systems have only slightly higher vinyl content.[41]

[34] A. W. Mayer, R. R. Hampton, and J. A. Davison, *Rubber Chem. Technol.*, 1953, **26**, 522.

[35] F. C. Foster and J. L. Bender, 'Advances in Chemistry', Series No. 19, A.C.S., 1957, 26.

[36] A. Rembaum, F. R. Ells, R. C. Morrow, and A. V. Tobolsky, *J. Polymer Sci.*, 1962, **61**, 155.

[37] T. L. Brown, *Adv. Organometallic Chem.*, 1965, **3**, 365.

[38] F. Schué and S. Bywater, *Polymer*, 1973, **14**, 594.

[39] S. Bywater, 'Progress in Polymer Science', ed. A. D. Jenkins, Vol. 4, Pergamon Press, 1975, 27.

[40] I. Kuntz and A. Greber, *J. Polymer Sci.*, 1960, **42**, 299.

[41] H. L. Hsieh, *J. Polymer Sci. A*, 1965, **3**, 181.

Even small amounts of polar solvents have a profound effect on the structure of the PBD's formed. Figure 1 shows how the vinyl content of PBD increases with the amount of polar component added to a hydrocarbon solvent; the rate of increase is clearly dependent on its solvating power.[42] Other authors[15] have studied the effect of THF on PBD structure over the complete range of solvent compositions and shown that the initial rapid increase in vinyl structure soon levels off, only increasing from 61% in 10% v/v solution to 79% in pure THF.

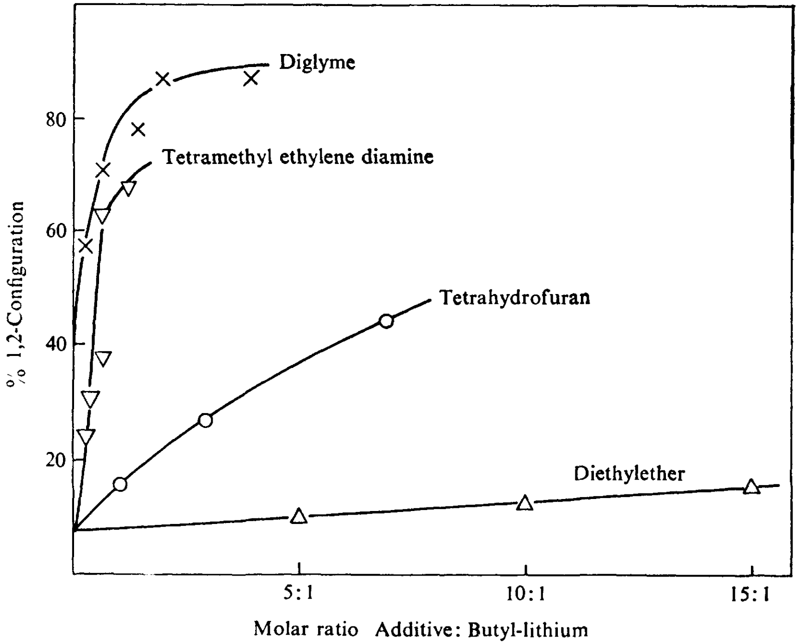

Figure 1 *Effect of polar additives on the structure of polybutadiene.*
Reproduced by permission from *J. Inst. Rubber Ind.*, (*A*), 1968, **6**, 3407.]

The increase in the rate of polymerization, and particularly the rate of initiation, observed on addition of polar solvents is caused by preferential solvation of the active ends, thereby enhancing the dissociation of monomeric ion pairs as well as increasing their concentration by reducing the association number of the alkyl lithium. For example, n-butyl lithium which is hexameric in hexane, is tetrameric in diethylether and probably dimeric in THF.[43]

C. Kinetics of Polymerization.—*Hydrocarbon Solvents.* The kinetics of polymerization is complicated by the fact that initiation and propagation take place

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[42] E. W. Duck and M. Locke, *J. Inst. Rubber Ind.* (*A*), 1968, **6**, 3407.
[43] P. West and R. Waack, *J. Amer. Chem. Soc.*, 1967, **89**, 4395.

concurrently, although the rate of initiation may be enhanced by suitable choice of alkyl lithium. Hsieh[44] has shown that the order of reactivity towards dienes is $Bu^s > Pr^i > Bu^t > Bu^i > Bu^n$, and that the faster initiator gives the more monodisperse product.[45]

The rate of initiation is always proportional to the monomer concentration,[44] whereas its dependence on catalyst is determined by the solvent; the order of initiation of isoprene by n-butyl-lithium is fractional in benzene,[45] but first order in hexane.[46] The latter relationship cannot be explained as initiation by monomeric initiator in equilibrium with hexameric aggregates, and direct addition of the monomer to the aggregate to form a mixed association [equation (13)] has

$$(RLi)_6 + M \rightarrow [(RLi)_5RMLi] \tag{13}$$

been suggested. Since there is some evidence that these are more reactive than the original hexamer,[47] autocatalysis of the initiation process can occur. Alternatively, the aggregation of initiator may be suppressed in the presence of polymeric ion pairs in favour of cross association,[48] and the inadvertent presence of other lithium salts such as alkoxide has also been proposed as a cause of breakdown of the initiator complexes.[49]

The propagation reaction is also first order in monomer, but in aliphatic solvents is fractional with respect to the propagating species. More recent estimates of this latter value centre around a quarter,[50] and again a correlation can be sought between this and the association number. Unfortunately, the two estimates attempted have given two different numbers; Morton *et al.*[50] obtain a value of two, whereas Worsfold and Bywater[51] find a figure of four with no evidence of dissociation over a wide range of dilution. A simple relation between reaction order and degree of association would only exist if the monomeric species were the sole active species. Hsieh and Glaze[52] have speculated that butadiene might complex with the aggregates before dissociation and addition occurs.

Polar Solvents. Addition of polar substances to hydrocarbon solutions of alkyl lithium increases the polar character of the species present, as evinced by a sharp increase in electrical conductivity,[53] and, although even in pure THF alkyl lithium is still principally dimerically associated, the formation of monomeric ion pairs is enhanced.

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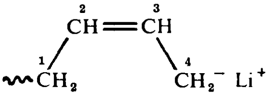
[44] H. L. Hsieh, *J. Polymer Sci. A*, 1965, **3**, 153, 163, 173.
[45] H. L. Hsieh and O. F. McKinney, *J. Polymer Sci. B*, 1966, **4**, 843.
[46] J. E. L. Roovers and S. Bywater, *Macromolecules*, 1968, **1**, 328.
[47] S. Bywater and D. J. Worsfold, *J. Organometallic Chem.*, 1967, **10**, 1.
[48] I. A. Alexander and S. Bywater, *J. Polymer Sci., A*, 1968, **6**, 3407.
[49] A. F. Johnson and D. J. Worsfold, *J. Polymer Sci., A*, 1965, **3**, 449.
[50] M. Morton, L. J. Fetters, R. A. Pett, and J. F. Meier, *Macromolecules*, 1970, **3**, 327.
[51] D. J. Worsfold and S. Bywater, *Macromolecules*, 1972, **5**, 393.
[52] H. L. Hsieh and W. H. Glaze, *Rubber Chem. Technol.*, 1970, **43**, 22.
[53] A. Kh. Bagdasar'yan, V. M. Frolov, E. I. Tinyakova, and A. B. A. Dolgoplosk, *Proc. Acad. Sci. U.S.S.R.*, 1965, **162**, 582.

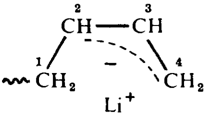
The kinetics of the initiation process, as distinct from the overall polymerization kinetics, have not been studied in detail. In THF, initiation is very fast, and once propagation takes place the high solvating power of the solvent breaks down any polybutadienyl lithium aggregates to monomeric ion pairs so that the rate of propagation is first order in catalyst and monomer.

The solvation of polystyryl–alkali metal salts in THF and other polar media has been studied by Szwarc and his colleagues,[54] who have established that a dynamic equilibrium exists between contact ion pairs, solvent separated ion pairs, and free ions. Although in THF the relative concentration of free ions is very small (~1 %), its propagation rate is about 800 times faster than that of the ion pairs so that polymerization is principally effected by this species. Rapid equilibration ensures that all chains participate equally in the polymerization process so that the polydispersity is low. No similar study has been made of the polydienyl lithium systems, but it may be expected that since there is less extensive charge delocalization the ionization would be lower, although the contribution of free ions to the polymerization process should still be significant. Recently, a study of cumyl potassium initiation in THF confirmed that propagation was almost entirely due to the free butadienyl anion.[55]

D. Mechanism of Anionic Polymerization.—Two basic observations have to be explained in any mechanistic picture developed for the alkali metal (alkyl) polymerization of butadiene, (i) the high 1,4-PBD's produced in bulk or inert solvent by lithium and its alkyls, and (ii) the high 1,2-PBD's prepared using other alkali metals under these conditions, and by all alkali metals and their derivatives when polar solvents are employed.



(6)



(7)

N.m.r. studies of the active ends in hydrocarbon media show them to exist exclusively as the 1,4-adduct (6) with a *cis–trans* ratio of about 3:1.[56] Addition of THF results in an upfield shift in the signal from the methine hydrogen on C-2, suggesting some contribution from the π-allyl structure (7). Although in THF the active centre is still primarily located on C-4, delocalization may be sufficient to allow attack by monomer at C-2 and cause vinylic addition. The virtually exclusive vinyl structure in PBD's prepared with lithium naphthalene cannot be explained in this way unless the regenerated naphthalene helps to delocalize the

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[54] M. Szwarc, 'Carbanions, Living Polymers and Electron Transfer Processes', Interscience, 1968.

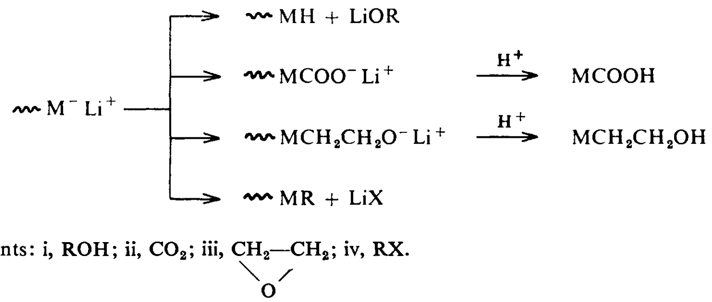
[55] A. Siove, P. Sigwalt and M. Fontanille, *Polymer*, 1975, **16**, 605.

[56] S. Brownstein, S. Bywater, and D. J. Worsfold, *Macromolecules*, 1973, **6**, 715.

charge. Bywater[39] has warned against looking for too close a parallelism between n.m.r. observations and the structure of the product, pointing out that in hydrocarbon solvents the former record the configuration in the aggregates whereas propagation is probably conducted by the unassociated species. Glaze *et al.*[57] examined the 1,4-addition product of t-butyl lithium and butadiene, neopentyl lithium, in ether solvents and confirmed that charge delocalization occurred. *cis–trans* Isomerization was slow in ether at 30 °C but considerably faster in THF.

There has been virtually no spectroscopic examination of polydiene anionic ends with other alkali metal counter ions, and inferences must again be drawn from Szwarc's results using polystyrene anions.[54] Here solvation of the counter ions falls off rapidly as their radii increase, and the active ends involving the larger cations are essentially contact ion pairs, particularly in hydrocarbon solvents. Thus with 'living' PBD's a terminal configuration analogous to (7) might be favoured as the cations could be stabilized by back donation from C-2 and C-4, and in part explain the predominance of vinyl structure in these PBD's.[39]

E. Termination.—After propagation has ceased, the active centres may be terminated by the addition of suitable reagents. Proton donors such as water or alcohol yield terminally non-functional PBD's[33] [Scheme 1]. Alternatively, carbon dioxide gives a carboxylate end group,[58] and ethylene oxide gives an alcoholate group.[59] Primary alkyl halide addition yields alkyl terminated PBD,[60] but β-hydrogen elimination reactions have been observed with secondary and tertiary halides.[61] Halogen terminated materials may be obtained by direct reaction with excess halogen or alkyldihalide, although significant



Scheme 1

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[57] W. H. Glaze, J. E. Hancock, J. Chaudhuri, M. L. Moore, and D. P. Duncan, *J. Organometallic Chem.*, 1973, **51**, 13.

[58] H. Brody, D. H. Richards, and M. Szwarc, *Chem. and Ind.* (*London*), 1958, 1473.

[59] D. H. Richards and M. Szwarc, *Trans. Faraday Soc.*, 1959, **55**, 1644.

[60] A. Davis, D. H. Richards, and N. F. Scilly, *Makromol. Chem.*, 1972, **152**, 121.

[61] A. Davis, D. H. Richards, and N. F. Scilly, *Makromol. Chem.*, 1972, **152**, 133.

amounts of Wurtz coupled product result due to the rapidity of the reaction.[62] This may be minimized by converting the 'living' polymer into its Grignard analogue before terminating.[62] The latter technique may also be employed to avoid ketone forming side reactions in the carbon dioxide terminating process.

Termination reactions are particularly important in the anionic preparation of telechelic liquid PBD's. These are low molecular weight (~3000) PBD's with terminal functional groups which can be cross-linked in a controlled manner by reaction with polyfunctional reagents such as isocyanates. Such systems have been comprehensively reviewed.[63]

F. Solution SBR's.—The development of emulsion SBR's spurred further investigation into the preparation of SBR's by anionic means. Products from these processes are called solution SBR's.

Because a high 1,4-conformation is required of the butadiene component, polymerization has to be carried out in hydrocarbon solvents. It was found, unexpectedly, that butadiene was preferentially polymerized and was virtually consumed before styrene took significant part in the reaction,[64] despite the faster rate of homopolymerization of styrene than butadiene. This phenomenon was interpreted as being caused by preferential solvation of the active ends by butadiene thereby preventing styrene access until the diene concentration was greatly reduced. Once accessibility had been achieved the polymerization process was accelerated. A different explanation was given by O'Driscoll and Kuntz[65] who developed a copolymerization equation based on the observation that the bulk of the active sites were present as non-propagating dimers. The two theories need not be mutually exclusive, however; the latter may be a formalization of the qualitative picture given by the former.

Whatever the detailed explanation, this phenomenon precludes the manufacture of SBR's in this way. This difficulty may be overcome in two ways; butadiene may be added to the system incrementally,[66] or a randomizing agent may be introduced.[67] The latter agent almost certainly acts as a preferential solvating agent, and polar solvents fall into this category although they adversely affect the microstructure. One of the more effective additives is lithium t-butoxide.[67]

Solution SBR's prepared for tyre purposes contain 20–25 % styrene and possess about 90% 1,4-structure (35—40% *cis*). They are superior to their emulsion counterparts in that the molecular weight distribution is controllable, and they contain no contaminants such as fatty or rosin additives. They are becoming increasingly important commercially. Nitrile rubbers cannot be prepared anionic-

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[62] F. J. Burgess and D. H. Richards, *Polymer*, 1976, **17**, 1020.
[63] D. M. French, *Rubber Chem. Technol.*, 1969, **42**, 71.
[64] A. F. Johnson and D. J. Worsfold, *Makromol. Chem.*, 1965, **85**, 273.
[65] K. F. O'Driscoll and I. Kuntz, *J. Polymer Sci.*, 1962, **61**, 19.
[66] D. J. Worsfold and S. Bywater, *Canad. J. Chem.*, 1960, **38**, 1891.
[67] U.S.P 3 094 512/1963.

ally as the nitrile group is susceptible to anionic attack and the stability of the acrylonitrile anion is too great to initiate butadiene polymerization.

G. Butadiene Block Copolymers (Thermoplastic Elastomers).—Block copolymers have been defined as 'polymers composed of molecules in which two or more polymeric segments of different chemical composition are attached end to end'.[68] Modern anionic processes have made their synthesis much more readily attainable; in particular they have led to the discovery and development of thermoplastic elastomers of the ABA type, where A represents a polymeric segment of high *Tg* (plastic component) and B represents a central polymeric segment of low *Tg* (elastomeric component). Because the entropy of mixing of polymers is low, the components are generally mutually incompatible and form a two phase system in which the plastic micelles are embedded in a rubber matrix.

At ambient temperatures, since the elastomeric chain ends are locked to the plastic micelles which act in place of chemical cross-links, the material exhibits elastomeric properties resembling those of a vulcanized rubber. As the temperature is raised through the *Tg* of the plastic component, however, the material exhibits thermoplastic properties and eventually melts. This means that, unlike normal rubber, a device made from these materials may be remoulded as required. The synthesis and properties of thermoplastic elastomers have been reviewed by Fetters.[69]

The first such materials developed, and currently the most important of this class were those derived from styrene and butadiene. Hereafter designated SBS, they are prepared anionically and consist of polystyrene segments of 10—15 000 molecular weight flanking polybutadiene segments of 50—100 000 molecular weight. Four distinct ways have been devised to prepare them.

Monofunctional Initiation. Styrene, butadiene and then styrene are added sequentially to an alkyl (usually sec-butyl) lithium initiator in hydrocarbon solvent. The time scale of initial styrene polymerization at 30 °C is about an hour, after which the butadiene block is formed in five to six hours. THF is added at this stage to speed the final styrene polymerization, and the system is then terminated with a proton donor and precipitated from methanol.

The main disadvantage of this procedure is that inadvertent introduction of extremely small quantities of impurities at any stage results in the formation of S or SB blocks. The latter contaminant has a deleterious effect on the properties of the SBS produced.[69]

Difunctional Initiation. Dianionic PBD is initially formed and styrene is then added to grow both terminal blocks simultaneously. The process has only two stages, but the common difunctional initiators are soluble only in polar solvents and

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[68] M. L. Huggins, P. Corradini, V. Desraux, O. Kratley, and H. Mark, *Polymer Letters*, 1968, 6, 257.

[69] L. J. Fetters, *J. Elastoplastics*, 1972, 4, 34.

consequently produce undesirable high 1,2-PBD's. Some seeding techniques have been attempted, and 1,4-dilithio-1,1,4,4,-tetraphenyl butane in hydrocarbon solvent containing 15% anisole has been used as initiator.[70] However, the lack of a suitable cheap difunctional initiator has prevented the development of this otherwise attractive synthetic route into a commercial process.

Monofunctional Initiation and Coupling. An S block is prepared on which butadiene is subsequently polymerized to half the chain length required. A coupling reaction is then carried out with a dihalide (RX_2) as indicated in equation (14).

$$S_n^-Li^+ + \frac{m}{2}B \rightarrow S_n\text{—}B_{m/2}^-Li^+ \xrightarrow{RX_2} S_n\text{—}B_{m/2}\text{—}R\text{—}B_{m/2}\text{—}S_n + 2LiX \qquad (14)$$

SB contamination can easily occur by inaccuracy in the titration or by a halogen–metal exchange side reaction. The latter can be minimized by adding THF after polymerization and raising the temperature to 40—50 °C before titrating. Phosgene has been found to be a very efficient linking agent.[71]

Direct Copolymerization. The preferential polymerization of butadiene in mixtures of butadiene and styrene may be used to prepare SBS polymers. A monofunctional initiator is used, initially with styrene, and then with a mixture of both monomers. The main disadvantage of this technique is that, during the polymerization of the mixture, styrene gets increasingly incorporated as the butadiene decreases, and a tapered segment of random composition separates the two essentially homopolymer blocks. This lessens the incompatibility of the two polymer components and the resulting phase blending gives materials with reduced tensile properties.

5 Polymerization by Alfin Catalysts

Alfin catalysts, discovered by Morton in 1947,[72] consist of a mixture of a sodium *al*koxide, sodium ole*fin* derivative and sodium chloride, the name being derived from the combination of the syllables in italic. The most active catalyst of this class is allylsodium, sodium isopropoxide and sodium chloride. The technological aspects of these systems have been recently reviewed.[73]

Polymerization is very rapid, resulting in a very high molecular weight PBD which possesses 75—80% *trans* and $<5\%$ *cis* structure. These molecular weights ($\sim 7 \times 10^6$) mean that the materials are difficult to process, but more recently it has been found that 1,4-dienes, particularly 1,4-dihydrobenzene or 1,4-dihydronaphthalene, are efficient molecular weight modifiers,[73] and [^{14}C] experiments have shown that one molecule of modifier is attached to each chain.

Morton investigated the system in some detail, and arrived at the following conclusions: (i) very few organo sodium derivatives exhibited catalytic activity

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[70] L. J. Fetters and M. Morton, *Macromolecules*, 1969, **2**, 463.

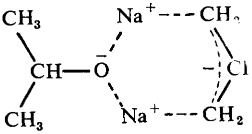
[71] M. Morton, R. F. Kammerick, and L. J. Fetters, *Macromolecules*, 1971, **4**, 11.

[72] A. A. Morton, E. E. Mogat, and R. L. Letsinger, *J. Amer. Chem. Soc.*, 1947, **69**, 650.

[73] R. Newburg, H. Greenberg, and T. Sato, *Rubber Chem. Technol.*, 1970, **43**, 333.

and, of these, allyl sodium was the most efficient, (ii) sodium isopropoxide was the most active of the alkoxides, (iii) maximum catalytic activity was obtained at equimolar allyl sodium and sodium isopropoxide, (iv) sodium chloride was a necessary component of the system, the activity of which was maximized when generated *in situ*, (v) the intrinsic viscosity did not increase with conversion, and (vi) the reaction was first order with respect to monomer, and each chain possessed an allyl group.

The equimolar relationship between allyl sodium and sodium isopropoxide led Morton to propose the cyclic co-ordination complex (8) adsorbed on to sodium chloride as the polymerization catalyst. He contrasted the rapid polymerization to give high *trans*-PBD with the slower polymerization by organo sodium catalysts to yield high 1,2-PBD, and thus suspected different mechanisms were in operation. Further, the lack of dependence of molecular weight on conversion led Morton to postulate a free radical mechanism in which the radicals were fixed on a lattice complex of sodium chloride and allyl sodium. The similarity in structures between Alfin catalysed and emulsion polymerized PBD's seemed to support this view.



(8)

Uelzmann,[74] however, proposed an anionic mechanism in which the isopropoxide adsorbed on to the sodium chloride lattice stabilized the growing anionic chain as illustrated for allyl sodium in (8). This hypothesis is now favoured as it explains the chain modifying capacity of the 1,4-dienes as being due to their action as hydride ion transfer agents. The constancy of molecular weight with conversion can then be ascribed to the action of a chain transfer process.

The role of the salt is clearly of importance. It has been shown that those which are catalytically active have a lattice constant between 2.81 and 3.29 Å.[75a] Indeed, Bykhovskii and Minsker[75b] have proposed that crystal defects which involve localized electrons (*e.g.* F centres) are sites of catalytic activity, but this is difficult to correlate with the critical role played by the organo sodium component. It is now accepted that, although this heterogeneous process is complex, the balance of evidence indicates that polymerization occurs by a form of anionic insertion mechanism.

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[74] H. Uelzmann, *Rubber Chem. Technol.*, 1959, **32**, 597.

[75] (*a*) L. Reich and A. Schindler, 'Polymerisation by Organometallic Compounds', Interscience, 1966, 406; (*b*) Bykhovskii and Minsker, *ibid.*, p. 420.

6 Polymerization by Transition Metal Catalysts

The discovery of the Ziegler–Natta (Z–N) catalytic systems[76,77] for the stereospecific polymerization of α-olefins and of dienes initiated a search for other effective transition metal catalysts. Z–N catalysts were defined as a combination of metal alkyls of Groups I to III with transition metal salts of Groups IV to VIII. In practice, however, the most efficient combinations were those in which an aluminium alkyl derivative were interacted with titanium, vanadium or cobalt salts.

So far as butadiene is concerned, successful catalysts of the Z–N type have been found as well as those which fall outside the Z–N patents. The distinction between Z–N and other catalyst systems has therefore become blurred and, apart from legalistic considerations, it seems unnecessary to compartmentalize them in this way. Hereinafter they will all be considered as transition metal catalysts.

Cooper and Vaughan[15] and, more recently, Ledwith and Sherrington[78] have discussed the mechanisms by which polymerizations catalysed by various transition metal systems occur, and this aspect will only be touched on in this review. The reactions between aluminium alkyls and transition metal compounds are very complex and have not been elucidated in many cases. They result in catalysts, some of which are soluble in hydrocarbon solvents, and those based on cobalt are very important for synthesizing high *cis*-PBD. Although it is difficult to generalize about systems involving aluminium alkyls, it appears that in many cases the initial reaction is the alkylation of the metal salt to form an unstable species which decomposes to liberate an alkyl radical and leave the metal in its reduced form [equation (15)]. These species may be further alkylated, and

$$AlR_3 + TiCl_4 \rightarrow AlR_2Cl + RTiCl_3 \rightarrow R\cdot + TiCl_3 \qquad (15)$$

polymerization is envisaged as taking place through co-ordination of the monomer at the missing site in the octahedral configuration of the transition metal caused by the missing ligand.

A further broad generalization may be made about catalytic systems involving aluminium alkyls. PBD's of the following structure are produced with the transition metal compounds listed: high *cis* $TiBr_4$, TiI_4, β-$TiCl_3$, cobalt compounds; high *trans* $TiCl_4$, $TiCl_3$ (α, γ, δ), vanadium halides; high vinyl, chromium and molybdenum compounds.

A. Titanium Compounds.—Addition of equimolar amounts of AlR_3 or AlR_2X to a solution of a Ti^{IV} compound in hydrocarbon solvent yields a precipitate of the Ti^{III} species[79] (the chloride in its β form). This may be further reduced to Ti^{II} by AlR_3, but not by AlR_2X.[80] The aluminium compounds are bound on to the

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

[77] G. Natta, *J. Polymer Sci.*, 1955, **16**, 143.

[78] A. Ledwith and D. C. Sherrington, 'Reactivities, Mechanism and Structure in Polymer Chemistry', eds. A. D. Jenkins and A. Ledwith, J. Wiley, 1974, Chap. 12.

[79] P. H. Moyer, *J. Polymer Sci. A*, 1965, **3**, 209.

[80] C. Beermann and H. Bestian, *Angew. Chem.*, 1959, **71**, 618.

Ti^{II} precipitate and play an essential role in its activity, and they may be added subsequently if the Ti^{III} compound has been prepared without their involvement. It is the nature of the Ti^{III} salt that determines the structure of the PBD formed rather than that of the reducing agent.

cis-1,4-*PBD's*. AlR_3–TiI_4 and analogous systems containing iodine can produce 95% *cis*-PBD's.[81] Systems such as AlR_3–$TiCl_2I_2$ and AlR_3–I_2–$TiCl_4$ are typical, and have the advantage over the tetraiodide that the titanium compounds are more soluble. These three formulations behave similarly because in each case any chloride is eliminated into the solvent, leaving the precipitate as TiI_3. They have the following features in common: (i) catalytic activity starts at Al:Ti = 1 and increases with this ratio to a maximum variously quoted at ratios of 1.5 to 3[82] and 5,[79] (ii) catalytic activity decreases as the polymerization proceeds, (iii) molecular weight increases with conversion and varies inversely with catalyst concentration, (iv) the *cis* content increases with decreasing catalyst concentration, reaching 95% at 10^{-3} molar in benzene; it is also maximized at Al:Ti ratios corresponding to maximum catalytic activity.

Electron donors such as di-isopropyl ether have been used to stabilize the catalyst,[83] and other recipes where aluminium alkyl has been replaced by aluminium hydride derivatives also yield high *cis*-PBD's.[84] The feature common to all these systems is, however, that the titanium is present as the tri-iodide.

trans-1,4-*PBD's*. The most efficient titanium catalysts for preparing the highly crystalline *trans*-PBD are those containing α-$TiCl_3$, which is produced by reaction of hydrogen on $TiCl_4$ at high temperatures.[85] Even in these systems, however, significant amounts of amorphous material are formed which can be ether extracted.

Vinyl-PBD's. Although titanium compounds have been used to prepare highly tactic 1,2-PBD's, the halides have to be excluded as they are 1,4-directing. The systems are generally homogeneous. $AlEt_3$–$Ti(O{-}Bu^n)_4$ gives a high isotactic vinyl product.[86,87] Interestingly, $Ti(NEt_2)_4$ yields high 1,2-PBD's with $AlEt_3$, $AlHCl_2OEt_2$ or $AlHCl_2NMe_2$; the last two produce syndiotactic material, whereas use of $AlEt_2Cl$ or $AlEtCl_2$ eliminates any vinylic addition and yields high *trans*-PBD.[88]

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[81] Belg. P. 551 851/1957.

[82] P. H. Moyer and M. H. Lehr, *J. Polymer Sci. A*, 1965, **3**, 217.

[83] J. F. Henderson, *J. Polymer Sci. C*, 1963, **4**, 233.

[84] W. Marconi, A. Mazzei, A. Araldi, and M. de Maldè, *J. Polymer Sci. A*, 1965, **3**, 735.

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[87] G. Natta, L. Porri, and A. Carbonaro, *Makromol. Chem.*, 1964, **77**, 126.

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B. Vanadium Compounds.—*trans*-1,4-*PBD's*. Vanadium halides in conjunction with AlR_3 or AlR_2X yield catalysts which are specific for *trans*-PBD's (>95%).[89] β or γ $TiCl_3$ may be added to VCl_3 before reaction with AlR_3 to give a catalyst with increased efficiency. Cooper,[90] experimenting with metal alkyls other than aluminium, has shown that the vinyl content of PBD increases at the expense of *trans* in the series Pb < Cd < Mg < Li < Na. Homogeneous catalysts can be prepared from $V(acac)_3$ (acac = acetylacetonate) or VCl_3 3THF and $AlEt_2Cl$;[91] at very high Al:V ratios they yield highly crystalline pure *trans*-PBD's, although their molecular weights are lower than those produced by heterogeneous catalysts.

C. Chromium and Molybdenum Compounds.—*Vinyl-PBD's*. Salts of both these metals with AlR_3 form catalysts which give high 1,2-PBD's. Chromium based catalysts yield product, however, in which the tactic component is <50%, whereas those based on molybdenum are more specific. $MoO_2(OR)_2$, $MoO(acac)_2$, and $Mo(acac)_3$ give a 95% vinyl product in which there is 75% syndiotactic material.[92]

π-Allyl complexes of chromium [$Cr(\pi\text{-allyl})_3$ and $Cr(\pi\text{-crotyl})_3$] polymerize butadiene without co-catalyst to give essentially pure 1,2-PBD.[93] However, if other transition metal halides are used as co-catalysts the structures of the resulting polymers are dramatically changed;[94] thus $NiCl_2$ or TiI_4 gives PBD possessing >90% *cis* structure, whereas $NiBr_2$ gives 95% *trans*-PBD.

D. Cobalt Compounds.—These compounds, with AlR_2Cl or $AlRCl_2$, form soluble catalysts which produce high *cis*-PBD's although the former co-catalyst requires water or HCl as an activator. With AlR_3 syndiotactic 1,2-PBD is formed.

cis-1,4-*PBD's*. The structure of the polymer formed with these catalysts is independent of the cobalt salt and is insensitive to the Al : Co ratio above 30 : 1. This is explained as an initial exchange occurring between the chloride of the aluminium species and the cobalt salt to yield $CoCl_2$ which is then alkylated to RCoCl. This decomposes to an alkyl radical and cobalt(I) chloride which is stabilized by complexation with the aluminium compound and which then becomes the active catalytic species.[94]

Lists of Co–Al catalytic systems have been made elsewhere,[15] and so will not be reproduced here. Apart from the properties mentioned above, all these cobalt catalysts have the following features in common: (i) the molecular weight of the product increases with time, and is related directly to the monomer concentration

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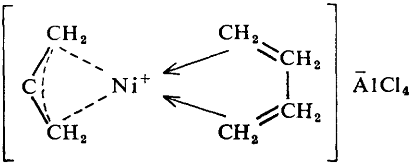
and inversely to the cobalt concentration, (ii) the rate of reaction is first order with monomer and cobalt concentrations, (iii) the polymerization may be carried out over a wide temperature range (−30 °C to +30 °C) without affecting stereospecificity.

Very high molecular weights can be obtained with these systems, and regulators, such as hydrogen, olefins, allenes or cyclooctadiene, have been used to reduce the chain length and yield an easily workable product.[95]

The catalyst $CoCl_2$–$AlCl_3$ is an entirely inorganic catalyst which forms high *cis*-PBD. It has been shown to have the structure $Co(AlCl_4)_2$, but it is more commonly used with thiophene which increases its activity.[96]

Vinyl-PBD's. Cobalt salts with AlR_3 form soluble catalysts in general, which produce highly syndiotactic 1,2-PBD's.[97] The amorphous region does not exceed 10% and the crystalline residue possesses exclusively 1,2-units. Again, a variety of cobalt compounds may be used in these systems, but their activities are lower than those of their analogues for *cis*-PBD and the molecular weights of the product are significantly less.

E. Nickel Compounds.—*cis- and trans*-1,4-*PBD's*. Normal σ-bonded nickel salts combined with $AlEt_2Cl$ catalyse butadiene polymerization to high *cis*-PBD (~85%), but not as efficiently as the cobalt complexes.[98] The main importance of nickel compounds as catalysts lies in the activity of the π-allyl nickel halides. These soluble compounds polymerize butadiene slowly without co-catalyst at a rate dependent on the square root of their concentration. Since they exist as dimers in hydrocarbon solution, it is clearly the dissociated form which is the active species.[99] The addition of Lewis acids such as $TiCl_4$ or $AlCl_3$ greatly increases their activity, and the kinetics becomes first order in catalyst.[100] The new catalytic complexes are almost certainly monomeric, and the initiating species is envisaged as (9), where butadiene is complexed in the S-*cis* form



(9)

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[95] C. Longrave, R. Castelli, and M. Ferraris, *Chimica e Industria*, 1962, **44**, 725.

[96] H. Scott, R. E. Frost, R. F. Bell, and D. E. O'Reilly, *J. Polymer Sci. A*, 1964, **2**, 3233.

[97] E. Susa, *J. Polymer Sci. C*, 1964, **4**, 387.

[98] W. M. Saltzman and L. J. Kuzma, *Rubber Chem. Technol.*, 1973, **46**, 1055.

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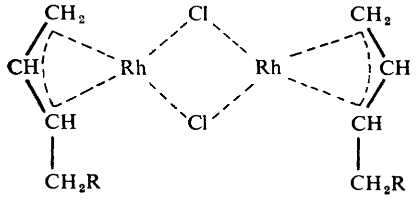
[100] T. Yashimoto, K. Kamatsu, R. Sakata, K. Yamamoto, Y. Takeuchi, A. Onishi, and K. Ueda, *Makromol. Chem.*, 1970, **139**, 61.

through both its double bonds.[101] The increased ionic character of (9) accounts for its increased activity.[102]

The nature of the halide in the catalyst system determines the structure of the PBD, whether the halide originates from the nickel salt or the co-catalyst. Chloride ions induce a high *cis* product whereas iodide ions direct the polymerization toward high *trans*-PBD. Bromide ligands give an intermediate structure with the *cis* form generally favoured, but in the majority of these systems the vinyl content is low ($\sim$3 %). The reactivity of the nickel catalysts increases in the order crotyl < methylallyl < allyl, and the configuration of the complex has been shown to be *syn*, independent of the microstructure of the PDB formed.[103,104]

F. Remaining Group VIII Elements.—Certain members of the second series of Group VIII polymerize butadiene in polar solvents such as water or ethanol. Although salts of ruthenium[105] and palladium[106] are catalytically active, rhodium compounds are outstanding in this regard and have consequently been most studied.

Aqueous rhodium nitrate polymerizes butadiene directly without benefit of additives, although other rhodium salts require the presence of a sulphate or sulphonate emulsifier, the structure of which is critical for the polymerization. Thus sodium lauryl sulphate is the sole active sulphate emulsifier, and sodium alkyl benzene sulphonates are active whereas sodium alkyl sulphonates are not.[107] It therefore appears that the emulsifier participates in the polymerization process, although the product is invariably high *trans*-PBD (>96 %). Free radical inhibitors have no effect, whereas 1,3-cyclohexadiene (molar ratio to Rh 20 : 1) increases the rate about twenty fold.[108] In contrast, 1,5-cyclooctadiene,[107] pyridine or EDTA[108] are powerful inhibitors.



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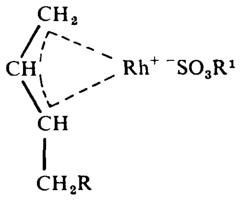

(11)

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[101] M. Gippin, *Ind. and Eng. Chem. (Product Res. and Development)*, 1965, **4**, 160.

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The polymerization mechanism probably involves co-ordination of the growing chain to form a π-allyl rhodium complex of low valency as the active species, possibly in the dimeric form (10).[109] The action of emulsifiers could then be to stabilize the monomeric species (11) in the micelle. Inhibitors probably act through competition with butadiene for the co-ordination sites on the rhodium ion.

G. Uranium Compounds.—There have been recent disclosures that uranium compounds polymerize butadiene homogeneously in hydrocarbon solvents to yield very high (99 %) *cis*-PBD. Tris(π-allyl)uranium halide produces this material in high yield, the activity being independent of the nature of the halide.[110] The catalytic activity may be improved by adding a Lewis acid, with $RAlCl_2$ being preferred owing to its solubility and availability. Alternatively, equally impressive results have been obtained using $U(OR)_4$ and $EtAlCl_2$ (or $AlEt_3$ and $AlBr_3$).[111]

The very high structural regularity allows fast and very extensive strain induced crystallization to occur, and results in a considerable improvement in processability and properties of the rubber.[111,112] These systems have not been examined kinetically as yet, but their products show considerable commercial promise.

H. Equibinary Polybutadienes.—Interest has recently developed in synthesizing PBD's possessing alternating structure involving two out of the three structural isomers. Thus *cis*-vinyl equibinary structure was claimed by Furukawa *et al.* for materials produced from the catalyst systems $MoCl_3(OR)_2$–$AlEt_3$(Al : Mo > 6)[11] and $Co(acac)_3$–$AlEt_3$–H_2O,[113] but ^{13}C n.m.r. studies later showed that the structural components were essentially random.[10,11]

Teyssié and co-workers produced equibinary *cis–trans*-PBD using a 2,6,10-dodecatriene-1,12-diylnickel-trifluoracetic acid system as catalyst,[102] but again its structural regularity was questioned by other workers.[8] Teyssié,[114] however, was able to show that the regularity depended on temperature and the nature of the solvent; the most regular alternating product being prepared in methylene chloride.

7 Conclusions

Butadiene can be polymerized in a variety of ways, but the structure of the polymer produced is very dependent on the technique employed. An indication of some of the structural variations which may be effected by the methods outlined

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[109] W. Cooper, *Ind. and Eng. Chem. (Product Res. and Development)*, 1970, **9**, 457.

[110] A. de Chirico, P. C. Lanzani, E. Raggi, and M. Bruzzone, *Makromol. Chem.*, 1974, **175**, 2021.

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[113] J. Furukawa, K. Haga, E. Kobayashi, J. Iseda, T. Joshimoto, and K. Sakamoto, *Polymer J. Japan*, 1971, **2**, 371.

[114] M. Julemont, E. Walckiers, R. Warin, and Ph. Teyssié, *Makromol. Chem.*, 1974, **175**, 1673.

herein is given in Table 2. In general the high 1,4-PBD's, favoured for their superior elastomeric properties, are manufactured commercially using alkyl lithium-initiated or transition metal-catalysed systems. The latter are based on titanium, cobalt or nickel.

Table 2 *Ranges of polybutadiene structures obtained by various polymerization techniques*

Method of Polymerization	*Catalyst System*	*Structure of Polymer/%*		
		cis-1,4	*trans*-1,4	1,2
Free Radical	Emulsion	20—3	60—74	22—16
Anionic	RLi Hydrocarbon solvent	34—38	56—50	10—12
Co-ordinated Anionic	Alfin	10—2	70—75	25—20
Transition Metal	Ti Halide AlR_3 or AlR_2X	80—94	15—1	9—3
	V Halide AlR_3 or AlR_2X	—	>95	1—5
	Mo Salts AlR_3	4	2—1	92—96
	Co Salts AlR_2Cl or $AlRCl_2$	93—98	3—1	4—1
	π-allyl NiCl AlX_3 or TiX_4	84—94	12—4	4—2