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Developments in Rubber Technology – 4

Edited by

A. WHELAN and K. S. LEE

ELSEVIER-APPLIED SCIENCE

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PREFACE

This volume, the fourth in a series which began in 1979, covers a greater variety of subjects than any previous single volume. The basis of selection has been topical interest; hence the tailor-making of polymers to develop specific properties, methods of improving compound processability and the use of rubbers in the oil industry are featured alongside a discussion of safety aspects.

We have again sought the cooperation of the foremost authorities on the chosen subjects and have been delighted at the response which has yielded a list of authors of international repute.

A.W.

K.S.L.

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Chapter 1

RECENT DEVELOPMENTS IN SYNTHETIC RUBBERS BY ANIONIC POLYMERIZATION

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1. INTRODUCTION

Although styrene-butadiene rubbers made in organic solvents (commonly called solution SBR) were introduced commercially in early 1960, their use has been limited to only a few structural varieties. Emulsion SBRs in blends with *cis*-BR (high *cis*-polybutadiene rubbers) were capable of meeting several performance requirements until the demand for low rolling resistance of tyre treads came to prominence in the 1970s. Then the potential of solution rubbers, with their much greater control of molecular structure, surfaced to meet the new requirements for improvements in rolling resistance and wet traction.

The objective of this chapter is to provide a survey of the technological developments in solution rubbers prepared by homogeneous anionic polymerization. Emphasis will be on butadiene and styrene monomers, and catalyst systems based on organolithiums and their complexes with Lewis bases plus some unpublished work on alkaline earths from the authors' laboratory. The rubbers thus obtained offer means for control of molecular structural features of polybutadiene and poly(butadiene-co-styrene) that directly relate to the functional properties of tyre rubbers.

2. POLYMER SYNTHESIS AND CHARACTERIZATION

2.1. Early Work on Diene Polymerizations

Early work bearing on organolithium-initiated diene polymerization was reported by Ziegler and co-workers in 1934.¹⁻³ It was demonstrated that the organolithium adds to the diene double bond to give an intermediate capable of reacting further with the diene.

The characteristics of the organolithium-initiated polymerization of the dienes was clearly established by Morton and co-workers. It was demonstrated that the polymerizations are of the 'living' type, which take place without a chain termination reaction in the absence of impurities.^{4,5} The implications of this behaviour in preparing polymers of controlled structure are well recognized today.

Homopolymers and copolymers with tailored-molecular structure, prepared using organolithium, have recently generated much interest because of their potential for improving rolling efficiency, wet traction and durability of tyre treads.

2.2. Organolithium Initiation of Dienes

Anionic polymerization requires unsaturated monomers having substituents that stabilize the negative charge on the active centre (electrophilic substituents) and initiators based on the most electro-positive elements. Among initiators for diene polymerizations, organolithiums are nearly ideal compounds. This stems from some of their main characteristics listed in Table 1. Solubility in non-polar solvents results from their covalent character and their ability to form electron-deficient bonding giving rise to associated forms, usually tetramers or hexamers.

TABLE 1
CHARACTERISTICS OF ORGANOLITHIUM POLYMERIZATION
CATALYSTS

-
- (1) Solubility in non-polar solvents.
 - (2) Associated structures.
 - (3) Reactivity varies with Lewis bases.
 - (4) High 1,4-polydienes.
 - (5) Living Polymerization.
 - (6) Control of molecular weight and molecular weight distribution.
 - (7) Versatility in solution polymerization.
-

TABLE 2
STRUCTURAL CONTROL IN SOLUTION STYRENE-BUTADIENE
RUBBERS USING ANIONIC CATALYST SYSTEMS

-
- (1) Composition.
 - (2) Monomer sequence distribution (random, tapered, block).
 - (3) Microstructure variation in polybutadiene microstructure (vinyl, *cis* and *trans*).
 - (4) Molecular weight and molecular weight distribution.
 - (5) Molecular chain architecture (linear or star).
 - (6) Addition of functional groups.
-

Lewis bases coordinate with the Li^+ ion, breaking up the aggregate. In general, complexing with Lewis bases results in increasing the reactivity of organolithiums and greatly alters, as discussed later in this chapter, the polydiene structure.

The most common Lewis bases used in organolithium-initiated polymerizations are aprotic amines and ethers. More strongly complexing agents include hexamethylphosphoramide, polyglycol dimethyl ethers, cyclic ethers (crown ethers),⁶ and dipiperidinoethane (DIPIP).⁷

An important feature of anionic polymerizations with organolithiums is that they can take place in the complete absence of a termination reaction. Organolithiums are stable species in hydrocarbon solvents at normal polymerization temperatures (20–50°C). This is the reason the polymers are commonly referred to as 'living polymers'. This special characteristic coupled with the association features of the propagating centre are mainly responsible for the high degree of structural control for diene rubbers prepared using butyllithium, as summarized in Table 2. In addition to control of polymer composition, control of molecular weight, molecular weight distribution, diene microstructure (geometric isomerism of diene units in the polymer chain), monomer sequence distribution, molecular chain architecture and chain end derivatization can conveniently be achieved. Thus, the use of alkylolithiums as polymerization catalysts offers a highly versatile method for molecular engineering of rubbers of controlled structures.

2.3. Microstructure Variations

Having two conjugated double bonds, butadiene can result in various isomeric structures in the polybutadiene chain, as shown in Fig. 1. When both double bonds participate in 1,4-addition, the remaining double bond in the polymer backbone can exist as two geometric

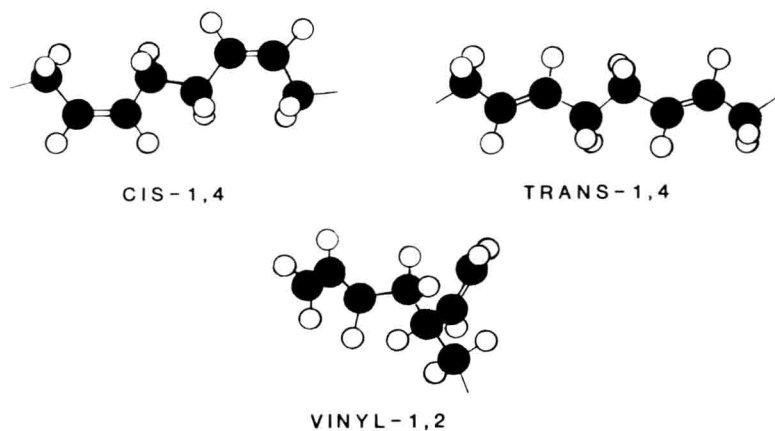


FIG. 1. Polybutadiene isomers.

isomers, namely *cis*-1,4- and *trans*-1,4-units. Addition across only one of the double bonds produces the vinyl or 1,2-structure. Three stereoisomers of 1,2-polybutadiene are possible: isotactic, syndiotactic and heterotactic (atactic). As far as is known, the homogeneous anionic polymerization of butadiene appears to have no effect on the stereoisomerism of the asymmetric carbon in the vinyl structure, in that only the atactic structure has been reported.⁸

Values of glass transition temperature (T_g) and crystalline melting temperature (T_m) for the various polybutadiene structures are given in Table 3. Crystallinity arising from chain structure regularity can occur

TABLE 3
GLASS TRANSITION TEMPERATURE AND
MELTING TEMPERATURE OF POLYBUTADIENES

<i>Polybutadiene</i>	T_m (°C)	T_g (°C)
<i>cis</i> -1,4	2	-113
<i>trans</i> -1,4	—	-88
Form I	55	—
Form II	145	—
Atactic-1,2	—	-4
Syndiotactic-1,2	156	—
Isotactic-1,2	128	—

in all of these forms. Only the atactic vinyl and *cis*-1,4-polybutadiene (*cis*-BR) are amorphous at room temperature in the relaxed state. It is possible, of course, to decrease crystallinity in polybutadienes by introducing irregularity in a random manner, for example by introducing mixed microstructures and/or styrene units that can interrupt crystallizable sequence lengths. Strain-induced crystallization may be achieved in polybutadienes with crystallizable sequences of suitable length under special conditions (Section 3.5.2).

The choice of solvent and/or polar modifier used for organolithium polymerizations greatly affects the chain microstructure of polydienes, comonomer sequence length distribution in styrene-butadiene copolymerizations, and the rate of polymerization. Generally, those modifiers (without bulky substituents) which make it possible to increase the rate of polymerization also result in a higher vinyl content and significantly alter the reactivity ratios for styrene and butadiene. In many circumstances, a more random and less 'blocky' copolymer is produced. On a molecular level, these effects are related to greater charge separation of the polybutadienyl or polystyryl carbanion and the Li⁺ cation.

The influence of polar modifier on the microstructure of polybutadiene prepared with butyllithium (BuLi) is summarized in Table 4. It

TABLE 4
EFFECT OF VARIOUS MODIFIERS ON VINYL CONTENT OF
POLYBUTADIENES

Modifier	Molar ratio Modifier/BuLi	Microstructure (%) ^a		
		Vinyl	<i>trans</i>	<i>cis</i>
None ^b	—	8	57	35
Triethylamine ^c	270	37	39	24
Diethyl ether ^b	6	21	50	29
THF ^b	1	35	40	25
TMEDA ^c	1	76	16	8
DIPIP ^d	1	99	1	—

^a Prepared in *n*-hexane at 20–30°C at [Bd]₀ = 0.5M and [BuLi]₀ = 2 × 10⁻⁴ M.

^b Morton, M., *Anionic Polymerization: Principles and Practice*, Academic Press, New York, 1983.

^c Ref. 11.

^d Ref. 7.

can be seen that the bidentate polar ligands, tetramethylethylenediamine (TMEDA) and DIPIP, are capable of producing polymers with high vinyl unsaturation. A vinyl content of almost 100% is obtained in the presence of DIPIP.⁹ Ura-neck¹⁰ and Antkowiak¹¹ have reported that in the presence of these polar modifiers lower polymerization temperatures favour higher amounts of vinyl structure. However, in the absence of polar modifiers the diene structure is only somewhat dependent on temperature. For the bidentate ligands, the magnitude of the temperature influence is greater than for the monodentate ligands.¹¹

Polydiene microstructure is also dependent on the ratio of concentrations of monomer to organolithium. This is true for both non-polar and polar media. As catalyst levels are reduced in a non-polar system, *cis*-1,4-values as high as 86% have been observed in high molecular weight polybutadienes prepared in the absence of any solvents. This compares with 96% *cis*-1,4-content in similarly prepared polyisoprenes. In the case of high-vinyl BRs (HVBRs) prepared with a polar modifier, such as DIPIP, a decrease in alkylolithium (RLi) concentration at constant ratio of DIPIP/RLi produces smaller amounts of vinyl structure.¹²

In addition to the normal 1,4- and 1,2-structures of polybutadiene, the use of certain polar modifiers, e.g. TMEDA and tetrahydrofuran (THF), can result in the formation of vinylcyclopentane units (Fig. 2).¹³⁻¹⁶ This cyclic structure can be as high as 45 wt% in VBRs prepared by the addition of butadiene at a rate such that intramolecular cyclization can compete effectively with chain propagation. No appreciable amounts of cyclic structure are found in VBRs prepared by batch polymerization.¹⁴ How this cyclic structure influences the dynamic mechanical properties needs to be studied.

As discussed above, the amount of 1,2-addition in polybutadiene rubbers (BRs) can be varied from 8 up to 100% depending on the type of modifier and conditions used in organolithium polymerizations. This process versatility provides an important way to control T_g of BR and SBR rubbers. Figure 3 shows the relationship between increasing vinyl



FIG. 2. Proposed mechanism of vinylcyclopentane formation in vinyl-BRs.

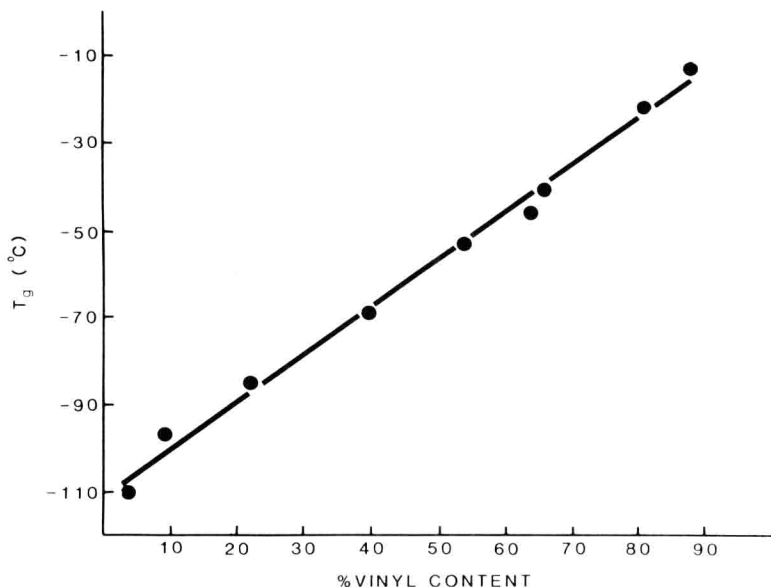


FIG. 3. Glass transition versus percentage vinyl content of polybutadienes.

content of BR (uncrosslinked) and T_g . As expected, T_g increases approximately linearly with an increase in the vinyl content of the polymer. In terms of the functional properties of tyre tread rubbers (discussed in Section 4), the T_g of the rubber can be considered an appropriate material property related to both wet traction and the abrasion resistance of a rubber.¹⁷

2.4. Control of Comonomer Sequence Distribution

Although the different isomers present in polybutadiene prepared by using alkyllithium catalysts have random placements, as shown by carbon-13 nuclear magnetic resonance (^{13}C NMR),¹⁸ solution SBRs have been produced with four basic types of sequence length of the comonomer units, as shown schematically in Fig. 4.

As previously mentioned, we are concerned in this chapter with essentially random copolymers of styrene and butadiene produced by solution polymerization. In terms of the distribution of styrene and butadiene units, random solution copolymers are considered as having only small variations in the sequence length distribution of the

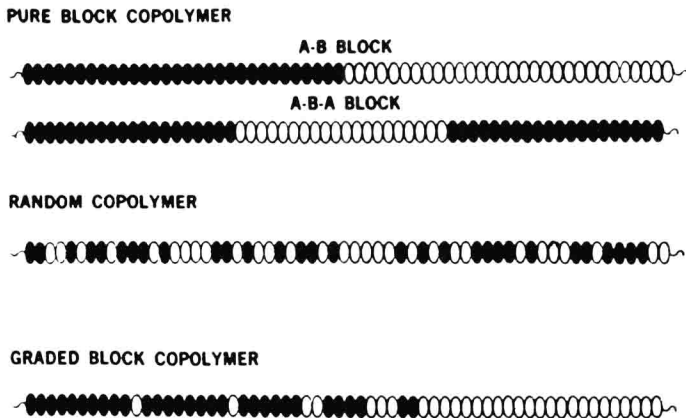


FIG. 4. Schematic representation of copolymer structures.

monomer units along the chain, and between different polymer molecules in a sample.¹⁹ This compares with uniform random copolymers in which the monomer distribution closely follows that expected from random statistical calculations and does not vary inter- and intra-molecularly—a situation that is approached in SBRs prepared by conventional free-radical emulsion polymerization (E-SBRs).

Several authors have reported that when butadiene and styrene are polymerized together, with an organolithium initiator in hydrocarbon solvent, there is a great preference for butadiene and relatively little styrene monomer is polymerized until butadiene is almost consumed.²⁰⁻²² This occurs even though the styrene monomer exhibits the faster rate of homopolymerization. At the latter stage of the copolymerization when the supply of butadiene nears depletion, then styrene begins to become incorporated into the chain. The resulting chain structure is referred to as a graded (or tapered) block copolymer having a block rich in butadiene.

Special polymerization approaches are necessary to prepare random solution SBRs with organolithium in hydrocarbon solvent. The main polymerization methods for producing random copolymers, or containing only short (non-blocky) styrene sequences, are given in Table 5. For convenience, the procedures are divided into those that control the polymerization process in order to maintain a high styrene/butadiene (Bd) ratio in the hydrocarbon media, and those that

TABLE 5
APPROACHES FOR PREPARATION OF RANDOM SOLUTION
STYRENE-BUTADIENE RUBBERS

<i>Control of monomer feed composition</i>	<i>Control of reactivity ratios</i>
Continuous Bd addition.	Polar organic modifiers (ethers and amines).
Continuous Bd and styrene addition.	Metal alkoxides High polymerization temperature.

use randomizers (polar modifiers) or very high polymerization temperatures to increase the ionic character of the carbon-Li bond. In this way, the reactivity ratios of butadiene and styrene become more favourable for copolymerization. Control of comonomer feed composition and the use of very high polymerization temperatures are typically used to produce SBRs having vinyl contents of about 10%, whereas the use of certain ethers and amines raises the vinyl content and, consequently, T_g . Ionic-type modifiers such as potassium *tert*-butoxide have been reported to produce random SBRs, at normal polymerization temperatures (20–50°C), having comparably low vinyl contents.²³

Some of the recent work in the authors' laboratory has shown that catalyst compositions of barium alkoxide salts combined with BuLi as well as with complexes of Mg-Al alkyls also result in low-vinyl solution SBRs (LVSBRS) in hydrocarbon solvent.²⁴ Such elastomers have a butadiene portion of *trans*-1,4-content as high as 90% and a vinyl content as low as 2%. The comonomer placement in the copolymers is predominantly random. The development and properties of these rubbers will be described more fully in Sections 3 and 4, respectively.

2.5. Characterization of Styrene Sequence Distribution in Solution Styrene-Butadiene Rubbers by Anionic Polymerization

Before the advent of NMR, qualitative information related to monomer sequence distribution was obtained primarily by the chemical method of Kolthoff.²⁵ In this procedure, the copolymer is oxidatively degraded at the double bonds of the polybutadiene segments. Polystyrene blocks are not attacked and are isolated and determined

gravimetrically as block styrene. Unfortunately, sequencing information pertaining to short segments of styrene are not obtainable by this method.

Nuclear magnetic resonance has proved to be an excellent method that provides detailed sequence data.²⁶⁻²⁸ Although only qualitative information on styrene sequence distribution was first possible from proton NMR spectra, recent advances in NMR techniques and spectrometers produce high-resolution spectra capable of providing quantitative information on sequence lengths of styrene in SBR. For example, using a 200 MHz superconducting NMR spectrometer, it is possible to distinguish styrene sequence lengths consisting of isolated units, styrene diads, styrene triads, short blocks of styrene (4-7 consecutive units) and long blocks of styrene (≥ 8 consecutive units). Proton NMR spectra (Fig. 5) of the styrene ring protons in two low vinyl (10%) solution SBRs (denoted as (A) and (B) in the figure) show the various types of styrene units present, indicated at I = isolated, D = diads, and polystyrene. It is interesting to note that NMR can

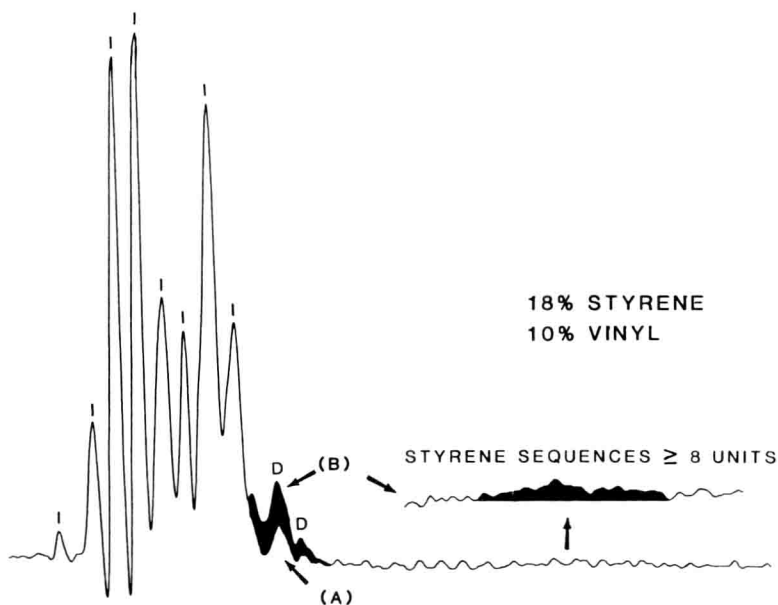


FIG. 5. Proton NMR spectra of two solution SBRs: polymer (A) more random than polymer (B). I, isolated styrene units; D, styrene diads.

TABLE 6

EFFECT OF STYRENE CONTENT AND MOLE RATIO OF TMEDA/BuLi ON THE AMOUNT OF STYRENE INCORPORATED AS LONG SEQUENCES IN SBR

Styrene (wt%)	TMEDA/BuLi	Vinyl (%)	Long Sequences of styrene	
			Polymer (wt%)	Total styrene (wt%)
20	0.6	45	0	0
25	0.6	45	1.0	4
30	0.6	45	2.1	7
50	0.6	45	19.5	39
50	1.2	60	0	0

distinguish one SBR as having an appreciable fraction of long sequences of styrene units.

Nuclear magnetic resonance data can provide detailed sequencing information that can help relate polymer structure to the particular polymerization method used to prepare solution SBRs. This can be demonstrated for the series of experimental medium vinyl solution SBRs shown in Table 6. Using BuLi complexed with TMEDA, in a batch polymerization of butadiene with styrene in cyclohexane at 65°C, the amount of 1,2-structure was maintained at about 45% and the styrene content in the polymer was varied from 20 to 50 wt%. For the medium-vinyl SBR (MVSBR) containing 20% or less styrene, the units of styrene are incorporated predominantly as isolated, diads and a small fraction of triads (in an amount that decreases with decreasing styrene content). As styrene content increases from 25 to 50 wt%, an increasing fraction of long sequences of styrene units is produced by this system. The last entry in Table 6 demonstrates that doubling the TMEDA concentration at constant BuLi raises the vinyl content as expected, and totally eliminates the long sequences of styrene in the polymer containing 50 wt% styrene. Thus, both the amount of styrene and TMEDA are crucial polymerization parameters that determine the particular styrene sequence distribution of solution SBRs.

2.6. Macrostructure Variations

In addition to polymer composition and microstructure, molecular weight, molecular weight distribution (MWD) and chain architecture (collectively referred to as polymer macrostructure) are considered to

be fundamental parameters affecting dynamic mechanical properties and the ability of rubber, in part, to be mixed, processed and fabricated into finished products. Anionic catalyst systems for preparing SBR and BR rubbers offer a variety of ways for effectively controlling polymer macrostructure.

As previously mentioned, anionic polymerization based on alkylolithiums involves essentially only two processes, initiation and propagation, because chain termination is absent. If all the growing chains are formed during a short time interval (i.e. initiation is fast relative to the propagation process) and if all the chains have equal opportunity to grow, then the resulting polymer will have a narrow molecular weight distribution. This feature can lead to low dynamic energy losses, which in tyre applications means low rolling resistance but greatly decreases the processability and results in viscoelastic behaviour that is characteristic of cold flow during long-term storage. The remedy for these deficiencies is usually found by altering the MWD and/or introducing a certain amount of controlled branching in the polymer molecule.

2.6.1. *Broadening MWD and Branching*

There are several approaches to broaden the MWD and introduce chain branches. The most commonly used are procedures that affect the initiation process,²⁹ and the use of branching comonomers such as divinylbenzene (DVB)³⁰ and chain end linking (coupling). The latter process has been widely used for coupling non-terminated chain ends with a variety of multifunctional organic and inorganic coupling agents. Examples of coupling agents are diesters, diketones, multifunctional vinyl compounds and metal halides. With respect to coupling of polymer chains bearing one reactive carbanion per chain, the number of branches will be controlled by the functionality of the coupling agent. For coupling agents that join chains by a polymer-halogen exchange reaction, the number of branches will be equal to or less than the number of halogen atoms of the coupling agent. When the coupling agent is a branching monomer such as DVB, which is capable of participating in both polymerization with itself and chain end linking, star polymers having as many as 30 branches (depending on reaction stoichiometry and conditions) have been produced.

Another approach to introduce branching is by the use of polyfunctional initiators. These initiators are based upon the reaction of an