New perfectly difunctional organolithium initiators for block copolymer synthesis: 2. Difunctional polymers of dienes and of their triblocks copolymers with styrene

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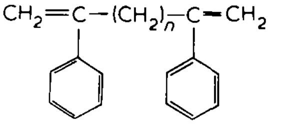
New organodilithium initiators were prepared in a hydrocarbon solvent in the absence of any polar additive. Although these initiators are insoluble when they are synthesized, they may be easily purified and reacted with dienes to give perfectly telechelic polydienes having unimodal distributions and low dispersity. A good agreement between experimental and theoretical molecular weights was observed. The polymer microstructures were similar to those of polymers initiated by butyllithium in the same solvent. Triblock thermoplastic elastomers were also prepared, the characteristics of which are given. The mechanical properties of a S.B.S. sample support also the claim of a good initiating ability and difunctionality of these initiators.

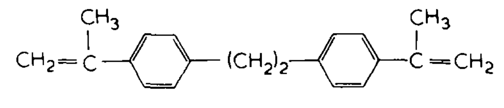
Keywords Lithium organic compounds; copolymer; synthesis; dienes; styrene; microstructure

INTRODUCTION

In a previous paper[1] we described the synthesis of new difunctional organolithium initiators. These compounds are obtained by addition of an excess of butyl lithium (sec- or tert) to a precursor in a hydrocarbon solvent at 30°C, in the absence of any polar additive. The precursors are of two types, one with α-alkylstyrene groups (A) and the other with α-methylstyrene groups (**B**).



A



B

In both cases there is slow formation of a dark red precipitate (after 3 h) that is nearly complete in 24 h. The precipitate is filtered and washed with hexane to eliminate the soluble monofunctional derivatives. The solubilization of the dicarbanionic species is made by addition of a monomer able to react with them. In the case of the synthesis of difunctional living polymers of dienes, seeds of low molecular weight are first prepared by adding an hexane solution of the diene to the initiator. For example, seeds of $\bar{M}_n$ about 3000 were obtained in ~15 min (starting from precursor A) and the initiator dissolved completely under stirring of the solution. These seeds are quite stable and lead to polymers with narrow molecular weight distributions that may be either functionalized or used for the synthesis of block copolymers.

In this paper we describe some results relative to polymers obtained with these compounds in order to verify their functionality, their molecular weight distribution and their stereoregularity. We also prepared some triblock thermoplastic elastomers (styrene-b-isoprene) or (styrene-b-butadiene) the characteristics of which are also given.

EXPERIMENTAL

The synthesis of the dilithium seeds has been described in Part I. The polymerizations or copolymerizations were carried out under vacuum in all glass apparatus equipped with break-seals. The monomers and solvents were purified according to the standard methods used in our laboratory[2,3]. The synthesis of the block copolymers was made by adding a solution of styrene in tetrahydrofuran to an hexane solution of the polydiene in order to accelerate the initiation of the styrene block (10–15 vol % of THF).

Gel permeation chromatograms were obtained with a Waters instrument equipped with four styragel columns (10^5–10^4–10^3–200 Å). Solutions containing 0.7 wt % of the polymers in THF were used at a flow rate of 2 ml min^{-1} and at room temperature.

Some samples were studied on four microstyragel columns (10^6–10^5–10^4–10^3) at 30°C. Solutions containing 0.17 wt % of polymers in THF were used at a flow rate of 2 ml min^{-1}.

The microstructure of some polyisoprene samples was investigated by ^{1}H and ^{13}C n.m.r. spectroscopy respectively at 100 MHz and 25,15 MHz on Varian XL-100 and JEOL PS-100 spectrometers (solutions 5–10 % w/v in $CDCl_3$ or C_6D_6 at 60°C).

The theoretical molecular weight was calculated

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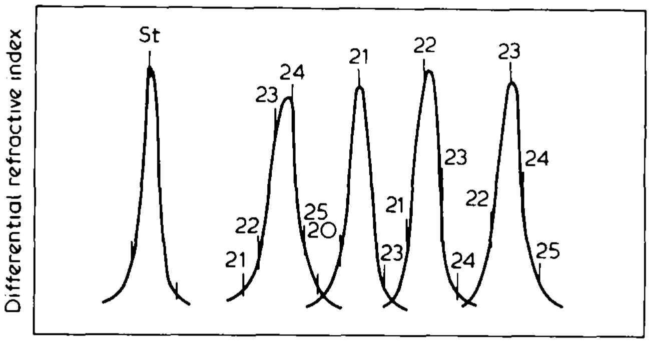

Figure 1 G.p.c. curves (in THF) for polyisoprene samples (St = standard polystyrene) $\bar{M}_w/\bar{M}_n$ = 1.04

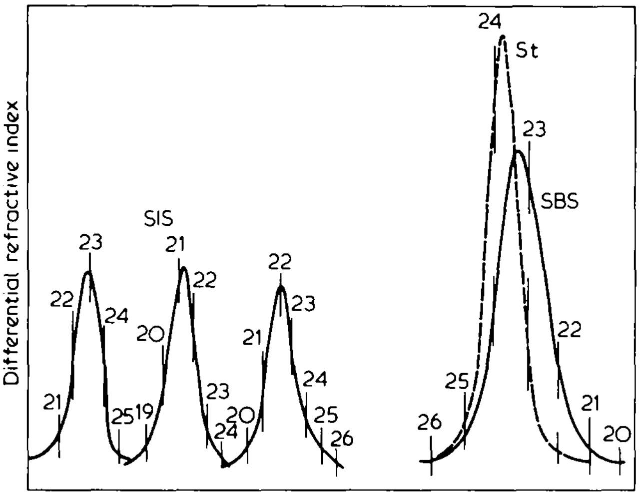

Figure 2 G.p.c. curves (in THF) for triblock copolymers (styrene-*b* isoprene) (SIS) and a triblock copolymer (styrene-*b* butadiene) (SBS) (St = standard polystyrene)

according to $\bar{M}_n = 2\ m/c$, where *m* denotes the amount of monomer (in g) and *c* denotes the amount of active species in moles. *m* was measured by gravimetry and *c* was determined by a spectrophotometric method using $\varepsilon_{290\ \mathrm{nm}} = 6000\ \mathrm{mol}^{-1}.\ 1\ \mathrm{cm}^{-1}$ at the stable isosbestic point of polyisoprenyllithium spectra. Determinations in our laboratory gave a value of 6000 ± 100 and Bywater found 6050[4]. However, one should be aware that both the calculated and the osmotic molecular weights are liable to errors of the order of 5%.

Mechanical properties of the SBS sample were examined at various temperatures and were compared to those of a KRATON 1101. The block copolymers were roll milled at 165°–170°C to ensure homogeneity and then compression moulded at 190°C. After compression moulding, both stuck tenaciously to the aluminium foil inserts. The aluminium foil was removed with a 5% aqueous NaOH solution. The moulded plaques were then examined for mechanical properties. Shore hardness was measured according to ASTM D-2240 and tensile properties according to ASTM D-412 on die C dumbbells (1 in span) tested at 20 in min^{-1}.

Verification of the difunctionality of polyisoprenyllithium

The suitability of difunctional initiators for the synthesis of triblock copolymers is not easy to prove.

An identification of the structure of the initiators and particularly their Li content is not sufficient to prove their efficiency for the synthesis of living polydienes having two equireactive living ends, that are suitable for the synthesis of ABA triblock copolymers. If the two organolithium groups have not both reacted (and particularly if one end is less reactive), the initiation of the second monomer may be incomplete and AB diblocks may be also formed, that have a marked effect on tensile strength.

However, if this occurs, the molecular weight distribution of the polymer should be bimodal with the highest molecular weight about the double of the lowest one.

The g.p.c. curves for a series of polyisoprenes are given in *Figure 1*. They show no trace of lower molecular weight species. This is consistent with the u.v. spectra of the living polymers that shows no u.v. absorption coming from the organolithium initiators.

The g.p.c. curves for a series of triblock thermoplastic elastomers are given in *Figure 2*. No trace of low molecular weight compound is observed.

We have also compared the experimental $\bar{M}_n$ obtained by osmometry with those calculated from the weight of monomer consumed *m* and the amount of living ends *c* ($\bar{M}_n = 2\ m/c$). The results are satisfactory as shown in *Table 1*, where A and B represent the two types of precursors respectively. This agreement is also visualized in *Figure 3* where theoretical and experimental values fall on a straight line within experimental errors.

The $\bar{M}_w/\bar{M}_n$ determined using g.p.c. given in *Table 1* was calculated according to Crammond *et al.*[5] without correction of axial dispersion and these values are overestimated. The chromatograms were analysed at each half count by planimetry or weighing. From these data, a cumulative weight curve was constructed. The cumulative weight data were plotted on normal probability paper as shown in *Figure 4*. A linear plot thus obtained up to 95% shows that the molecular weights are distributed according to a single normal law and therefore that one

Table 1 Comparison of theoretical and experimental molecular weights of various polymer samples

Initiator prepared from precursor	Polymer	Theoretical	Experimental $\bar{M}_n$ (osm.)	$\bar{M}_w/\bar{M}_n$ (g.p.c.)[a]
A	Polyisoprene	7 800	7 000[b]	–
	"	44 500	47 000	1.4
	"	220 000	230 000	1.25
	"	132 000	132 000	1.28
	"	71 500	73 000	–
B	Polyisoprene	27 000	29 000	1.32
		52 000	54 000	1.27
		110 000	105 000	1.29
A	SIS triblock[c]	95 000	93 000	1.37
	"	220 000	210 000	1.40
		150 000	145 000	1.50
A	SBS triblock[d]	–	82 000	1.36

[a] Determined according to Crammond *et al.*[5] See text
[b] Determined by vapour pressure
[c] The dispersities of the elastomeric central blocks were respectively 1.30; 1.22; 1.29
[d] Sample prepared in order to study the mechanical properties. The amount of polymer (30 g) and the volume of the apparatus did not allow a u.v. titration

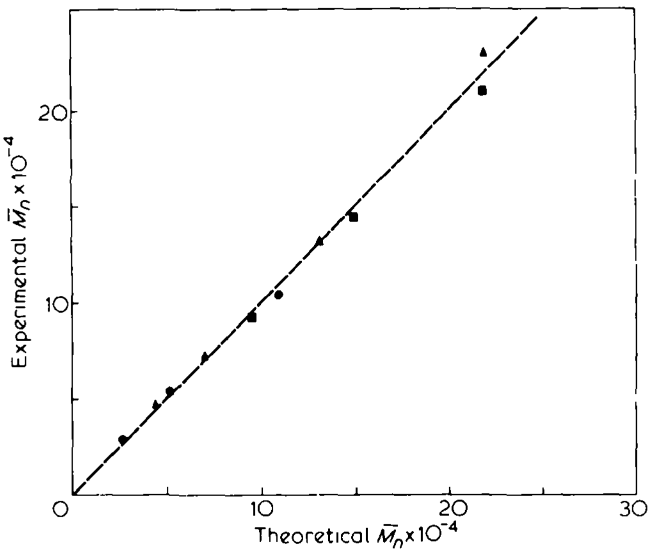

Figure 3 Relationship between experimental and theoretical $\bar{M}_n$. ▲, polyisoprene obtained from precursor A; ●, polyisoprene obtained from precursor B; ■, poly(styrene-b isoprene) triblock copolymers obtained from precursor A

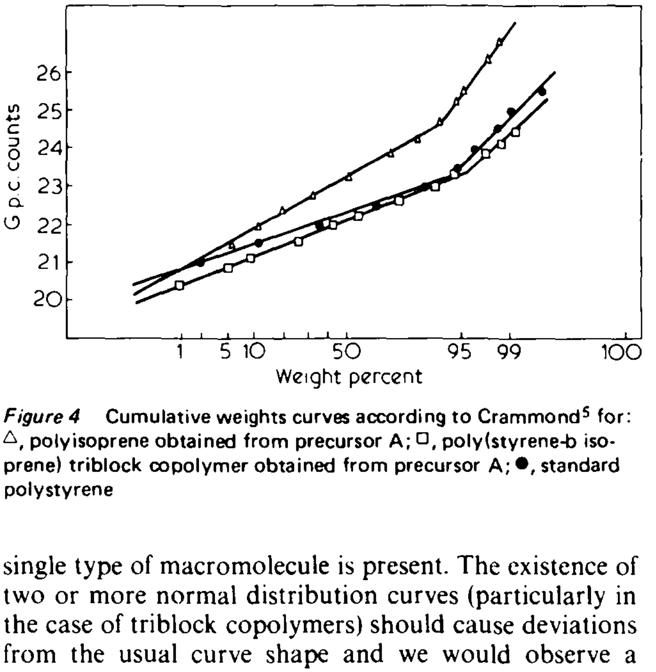

Figure 4 Cumulative weights curves according to Crammond[5] for: △, polyisoprene obtained from precursor A; □, poly(styrene-b isoprene) triblock copolymer obtained from precursor A; ●, standard polystyrene

single type of macromolecule is present. The existence of two or more normal distribution curves (particularly in the case of triblock copolymers) should cause deviations from the usual curve shape and we would observe a double inflection of the plot on probability paper. However, when the difference between the two means is small a single inflection will be observed. Deviation from linearity above 95% (also observed for a standard monodisperse polystyrene) might be due to inaccuracies of measurement. Such types of linear plots were obtained for all samples and this shows that the molecular weights are distributed according to a single normal relationship.

In spite of the fact that Crammond's method can reveal the presence of several normal distributions we looked for a more sophisticated method giving a more accurate dispersity determination. We compared two samples, the first being a standard polystyrene supplied by Waters Associates (standard n 41995; $\bar{M}_n$ osmo = 111000: $\bar{M}_w/\bar{M}_n = 1.01$) and the second one a SBS triblock copolymer prepared by us and already studied by Crammond's method. In this case, without axial dispersion correction and according to Crammond's method a dispersity of 1.17 was observed for the standard and 1.36 for the copolymer (elution on 4 styragel columns). For the same standard polymer, on microstyragel columns, with axial dispersion and concentration effect correction (Benoit's universal calibration law), we obtained a dispersity of 1.04. With the SBS triblock copolymer (which in *Table 1* is given with a dispersity of 1.36) we obtained a value of 1.15. In conclusion, the values given in *Table 1* are greater than the real values which are probably often lower than 1.1.

According to all these results, we may say that although these initiators are insoluble when they are synthesized, they react easily with dienes to give perfectly telechelic polydienes having a low poly dispersity for molecular weights from 20000 to 200000, and that they are well suited for the synthesis of ABA triblock copolymers where B is a polydiene.

Microstructure of the polyisoprene blocks

It is well known that the chain microstructure of the polydiene block in a ABA copolymer influences the elastomeric properties, *cis*-1,4 polydienes being preferred. But if the side vinyl content (1,2 or 3,4 units) is reasonably low (<20%) a mixed *cis* and *trans*-1,4 structure may still be satisfactory. It was important to study the chain microstructure of our polyisoprene samples.

For the determination of the microstructure, owing to the fact, that the i.r. method gives always a higher percentage of *cis*-1,4 units[6] we preferred to use ^{13}C n.m.r. and ^{1}H n.m.r. spectroscopy which give a more accurate estimate of the molecular architecture of polymers with low vinyl content. We studied the structures of samples obtained by using our two difunctional organolithium compounds and compared them with those of polyisoprenes reported in the literature. It may be said that low molecular weight polyisoprenes have a structure containing ~70% of *cis* 1,4 units which does not change greatly over a large initiator concentration range. However, for very high molecular weights the *cis*-1,4 content may rise by 95%[7,8]. Our samples had molecular weights between 20000 and 200000.

The ^{13}C and ^{1}H n.m.r. spectra were interpreted according to previously reported assignments[9-12] and the microstructure determined by means of these two methods are in good agreement as shown in *Table 2*. These values are close to those reported in the literature[14,15] and determined by similar methods.

To illustrate the differences given by i.r. and n.m.r. measurements one sample of telechelic polyisoprene ($\bar{M}_n$ = 132000) was studied by means of i.r. spectrophotometry according to [13]. These results are given in *Table 2*. We may notice that the i.r. microstructure

Table 2 Microstructure of various polyisoprenes

Sample initiated by	$\bar{M}_n$ osm.	*cis*-1,4 %	*trans*-1,4 %	3,4 %	Method of measurement
BuLi ref. 14		92.6			i.r.
ref. 15		75	20	5	^{1}H n.m.r.
Precursor A		94	0	4	i.r.
	132000	73	21	6	^{1}H n.m.r.
		70	20	10	^{13}C n.m.r.
Precursor A	73000	72	23	5	^{1}H n.m.r.
Precursor B	29000	70	23	7	"

Table 3 Comparison of properties of SBS block copolymers (compression molded at 190°C)

	Triblock prepared with precursor A	Kraton* 1101
% Polystyrene	27	30
$\bar{M}_n$	82 000	–
Breaking strength (Kg cm^{-2}), 23°C	240	240
100% modulus, 23°C	17.5	13.3
Breaking elongation 23°C (%)	1 060	1090
Shore hardness: 23°C	64 A	71 A
70°C	55 A	55 A
100°C	40 A	33 A
Permanent set (%) after 30 min at 100% extension: 23°C	9	10
70°C	21	26

* Shell Chemical Co.

value is very close to that found by Stearns for a polyisoprene sample initiated by nBuLi in *n*-pentane[14].

Mechanical properties of a thermoplastic polystyrene-polybutadiene-polystyrene (SBS) copolymer

A SBS triblock copolymer sample ($\bar{M}_n = 82\,000$) was prepared using precursor A and tested by courtesy of Hercules Co.

The results of this study are collected in *Table 3* where the mechanical properties are compared to those of a commercial Kraton 1101 sample. At room temperature, although its polystyrene content is lower, the mechanical properties of our sample are similar to those of the reference sample. But at all temperatures shore hardness and permanent set (after 30 min) are less affected by heat increase as seen in *Table 3*. A lower diblock content and/or a lower dispersity of the rigid end blocks might explain this behaviour. Our claim for a good initiating ability and difunctionality of these initiators is supported by these properties.

CONCLUSION

Insoluble organodilithium compounds prepared by addition at 30°C of an excess of sec- or tert-BuLi on α,ω-bis(phenyl vinylidenyl) alkanes or α,ω-diisopropenylalkanes, in apolar solvents and in the absence of any polar additive, are easily isolated and washed from soluble monolithium compounds. They initiate the polymerization of dienes giving telechelic seeds that are quite stable and lead to polymers having unimodal distributions and a low dispersity. A good agreement between experimental and theoretical molecular weights is observed. The microstructure of polyisoprenes was studied by ^{13}C and ^{1}H n.m.r. spectroscopy and was found similar to those of polymers initiated by BuLi in the same solvent as reported in the literature.

Triblock thermoplastic elastomers were prepared by forming polystyrene end blocks in the presence of 10–15% in volume of tetrahydrofuran. They have a narrow distribution and experimental molecular weights are in agreement with the calculated values. Mechanical properties of a SBS sample were compared to those of an industrial Kraton 1101 sample. Our sample (with a lower polystyrene content) had mechanical properties at room temperature nearly identical to those of the reference sample, but a better heat resistance (better retention of hardness) was found and also a smaller permanent set. This is probably the consequence of a lower diblock content and of a lower dispersity of the polystyrene end blocks. These properties support our claim of a good initiating ability and difunctionality of the initiators we have described.

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