Polymer Bulletin 2, 389–395 (1980)

Polymer Bulletin

Structural Regularity and Crystallization of Lithium Polyisoprene and Poly(Styrene-b-Isoprene-b-Styrene)

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Dedicated to Prof. Dr. G. Rehage on the occasion of his 60th birthday

Summary

By anionic polymerization in cyclohexane with sec-butyllithium as initiator polyisoprene and poly (styrene-b-isoprene-b-styrene) have been prepared with 92 mole % and 90 mole % cis-1,4 isoprene structural units respectively. From the ^{13}C NMR spectrum there is no evidence for chain reversals of the polyisoprene chain, which was claimed to prevent crystallization in lithium polyisoprenes in the unstretched state. By DSC it is shown that the polyisoprene sample crystallizes in the isotropic state at - 25°C. The block copolymer shows stress induced crystallization as demonstrated by temperature dependent stress-strain measurements.

Introduction

By anionic polymerization of dienes in hydrocarbon solvents with butyllithium as initiator polymers with a high content of cis - 1,4 units can be obtained under conditions of a high ratio of monomer to initiator concentration (GEBERT et al.) (WORSFOLD et al.). In the case of isoprene polymerization 92 % cis-1,4 content has been achieved, the rest being trans-1,4 - and 3,4 - units of about equal amount (WORSFOLD et al.). Polyisoprenes of such a high level of stereoregularity should show stress induced as well as isotropic crystallization behaviour. However, until recently it was believed, that lithium polyisoprenes do not crystallize in the unstretched state (SCHOENBERG et al.). It was claimed that chain reversals occur at the 3,4 - units in lithium polyisoprenes which disrupt the crystallization process. (BROCK et al.). However, no spectroscopic proof ot the occurence of irregular 4,1 - 3,4 head - head and 1,4 - 4,3 tail - tail linkages in these polymers was given since ^{13}C NMR spectroscopy the only spectroscopy method which can give evidence of these irregular linkages

0170-0839/80/0002/0389/$01.40

was not sufficiently sensitive at the time.

Experimental

Polyisoprene and poly(styrene-b-isoprene) were polymerized in cyclohexane with sec - butyllithium as initiator. In order to achieve a high cis-1,4 content in the polyisoprene chain the ratio of monomer concentration M and initiator concentration C_I was chosen sufficiently high (M = 5 moles/l, $C_I = 1,4\cdot10^{-4}$ moles/l) and the conversion was limited to less than 10 %. Three block poly(styrene-b-isoprene-b-styrene) was prepared by coupling of two block poly(styrene-b-isoprene) with $Si(CH_3)_2Cl_2$.The total cis-1,4 isoprene content, determined by ^{13}C NMR spectroscopy was 92 mole % for the homopolymer and 90 mole % for the block copolymer, the rest consisting of about equal amounts of trans - 1,4 - and 3,4 - units. The ^{13}C NMR spectrum of the polyisoprene sample is shown in fig. 1. The molecular weights $\bar{M}_n$ are $2\cdot10^5$ for polyisoprene and $1,2\cdot10^5$ for poly(isoprene-b-styrene-b-isoprene). The block copolymer contains 17 weight % styrene.

Irregular linkages

From ^{13}C NMR spectra of hydrogenated samples it has been shown that Alfin, radical and cobalt catalyzed polyisoprenes contain significant amounts of irregular 4,1 - 3,4 head - head and 1,4 - 4,3 tail - tail linkages. (TANAKA et al. 1976a). By the same technique the existence of 4,1 - 1,4 head - head, 1,4 - 4,1 tail - tail and 1,4 - 4,3 tail - tail linkages in polyisoprenes prepared with n - butyllithium - diethyl ether in pentane has been demonstrated (TANAKA et al. 1976b). They occur in very small amounts only and the corresponding small signals overlapped with other strong signals do not allow for a quantitative estimate in the spectra of the hydrogenated samples. In the ^{13}C spectra of unhydrogenated polyisoprenes an assignment was given for the methylene carbons of trans - and cis - units in head - to - head additions at 38.6 ppm and 31.4 ppm, respectively, and for the methylene carbons of both isomers in tail-tail linkages at 28.4 - 28.8 ppm (KHATACHATUROV et al). Applying the empirical chemical shift parameters for linear and branched alkanes (GRANT et al., LINDEMAN et al.) suitably adapted to polyisoprene one expects the resonances of methylene carbons C_4 of the cis - unit in cis-1,4 - 4,3 tail - tail linkages at 25.8 ppm and the resonance of methylene carbons C_1 of cis-1,4 units in cis-4,1 - 3,4 head - head linkages at 34.4 ppm (for numbering of carbons and assignments see fig. 1.)

Signals corresponding to these irregular linkages have been identified in the ^{13}C spectra of unhydrogenated polyisoprenes prepared with butyllithium in cyclohexane / tetrahydrofurane and Ziegler catalysts respectively (SCHÄFER).

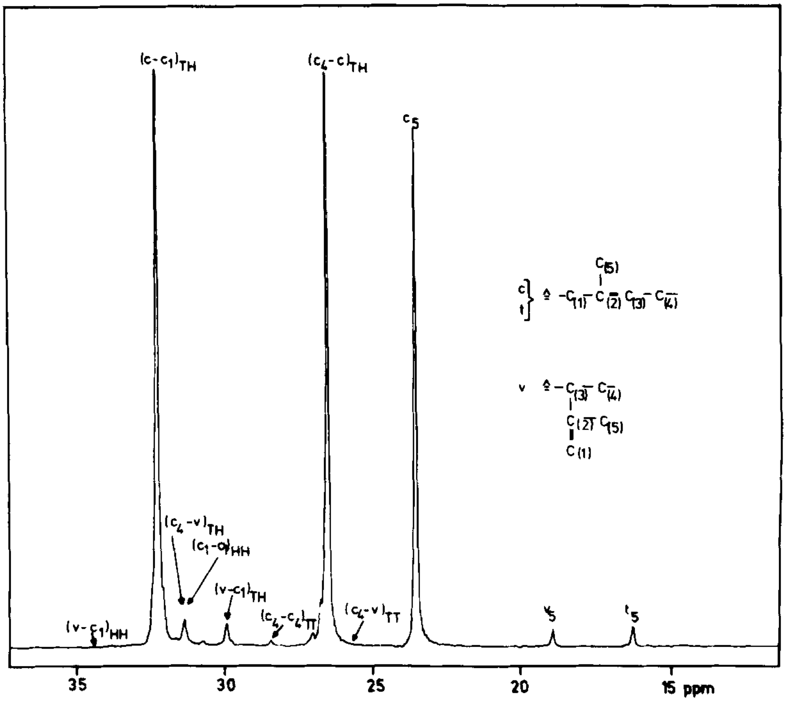

Figure 1: ^{13}C NMR spectrum of polyisoprene prepared with sec - Buli in cyclohexane (92 % cis - 1,4, 4 % trans - 1,4, 4 % 3,4). Assignment as defined in figure with H and T representing head and tail additions, respectively.

In the ^{13}C spectrum of a polyisoprene sample with 92 % cis - 1,4 prepared with sec-butyllithium in cyclohexane, which is shown in fig. 1., no signals at 25.8 ppm and 34.4 ppm arising from methylene carbons of cis - (1,4) - units in irregular enchainments of (1,4) - units in irregular enchainments of (1,4) and (3,4) units can be detected. On the other hand two signals of equal intensity can be distinguished at 31,4 ppm and 29.9 ppm which have be to assigned to C_4 methylene carbons of cis - 1,4 units in regular 3,4 - cis - 1,4 tail - head linkages and C_1 methylene carbons of cis - 1,4 units in regular cis - 1,4 - 3,4 tail - head linkages, respectively (GRONSKI et al.). The only irregular enchainments detected are tail-to-tail additions of 1,4 - units - nearly all of them being cis - 1,4 in this polymer - which give rise to a small signal at 28.4 ppm. From the relative intensities of this signal and the signals corresponding to regular cis-1,4 additions at 26.2 ppm and 32.4 ppm one estimates the content of tail-tail linkages of cis - 1,4 units to be about 0,5 %. The corresponding signal of the head - head cis - 1,4 linkage is hidden below the stronger C_4 methylene signal of cis - 1,4 units of regular 3,4-cis-1,4 linkages at 31.4 ppm. By a pyrolysis gas-chromatographie method it has been shown that some polyisoprenes e. g. those prepared by Alfin catalysts contain considerably more tail - tail 1,4 than head-head 1,4 enchainments. (HACKATHORN et al.). This difference can only be compensated by an equivalent amount of tail - tail 1,4 - 4,3 linkages where chain reversals occur. It can be seen in fig. 1. that there is no spectroscopic evidence for chain reversals occurring preferentially at 3,4 units in lithium polyisoprene. Neither does a relative enchainment of the signal at 31.4 ppm relative to the signal at 29.9 ppm indicate that head - head 1,4 linkages occur at significant higher frequency than tail - tail 1,4 linkages nor does a signal at 25.8 ppm where the resonances of the C_4 methylene groups of cis - 1,4 units in cis-1,4 - 4,3 enchainments are to be expected, point to a significant amount of these chain reversing diads. Thus it appears that in polyisoprenes prepared with Buli in hydrocarbon solvents all irregular linkages are distributed in a random way and the relative frequency of these irregular linkages, as estimated from the small content of 1,4 tail - tail linkages does not exceed 0,5 %.

Crystallization of polyisoprene

The sample of fig. 1. with 92 % cis-1,4 units was hold in a DSC - chamber at -25°C for 22 h. The subsequently taken DSC melting curve is shown in the upper part of fig. 2. and can be compared in the lower part to the DSC trace of natural rubber crystallized under the same conditions. The DSC curve of the lithium polyisoprene shows essentially the same melting behaviour as NR. The two different transitions which appear in fig. 2. have been attributed to different crystalline morphologies (EDWARDS).
From the relative areas of the two curves one obtains a relative degree of crystallinity of 47 % for the lithium polyisoprene. In fig. 3. the degree of crystallinity relative to natural rubber measured after crystallization at - 25°C for 22 h is plotted as a function of the cis - 1,4 content. Our result (Δ) has been plotted together with dilatomeric data of BROCK et al. for various Ziegler polyisoprenes (●) a polyisoprene prepared with butyllithium (▲) of

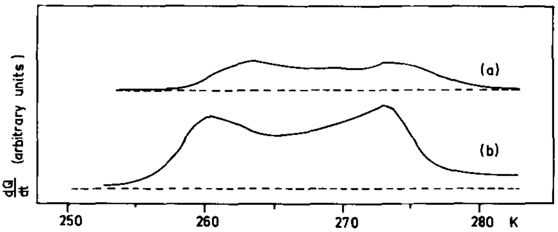

Figure 2:

Standardized DSC thermogram of
a) polyisoprene prepared with sec-Buli in cyclohexane (92 % cis - 1,4, 4 % trans-1,4, 4 % 3,4, 4.8 mg)
b) natural rubber (6,25 mg). Rate 10°C/min. Crystallization temperature - 25°C, crystallization time 22 h.

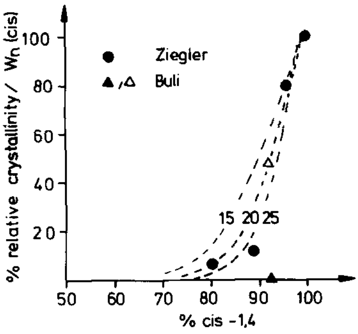

Figure 3:

Relative crystallinity of various polyisoprenes with respect to natural rubber: (● ▲) data from BROCK et al. (△) this work. Curves W_n (cis) represent calculated weight % of cis - 1,4 sequences containing at least n cis 1,4 units for n = 15, 20, 25.

similar cis-1,4 - content as our sample. The discrepancy between the two lithium polyisoprenes is simply explained by the overestimation of the cis-1,4 content of the older sample by means of infrared spectroscopy due to the nonadditivity of the extinction coefficients of cis and trans units (TANAKA 1971). This also explains the deviation of one of the Ziegler samples with a relatively high trans-1,4 content from the curve which joins the points of Ziegler samples with no trans content and our lithium polyisoprene. This curve has been calculated and represents the weight fraction W (cis) of pure cis - 1,4 sequences at least n = 20 units long. The curves corresponding to n = 15 and n = 25 are also shown in fig. 3. The satisfactory representation of the experimental points by a theoretical curve calculated under the assumption of a random distribution of the structural units indicates that the controlling factor of crystallization and crystallinity in polyisoprenes is given by the relative amount of randomly distributed 3,4 - and trans- 1,4 units and not, as recently suggested by FRIEDMAN et al., by the "correctness" of regular monomer addition.

Crystallization of poly(styrene-b-isoprene-b-styrene)

Since it is possible to prepare crystallizable polyisoprenes with high cis - 1,4 content by anionic polymerization the interesting opportunity is offered to synthesize poly(styrene-b-isoprene-b-styrene) with crystallizable polyisoprene middle block and well definded block length, composition and morphology. Unlike most other crystallizable block copolymers the morphology of these copolymers at normal temperature will be solely controlled by the incompatibility and composition of the components without interference of crystallization processes. Thus one can study independently the influence of block length and morphology on either isotropic crystallization or stress induced crystallization. In a first step towards this aim we studied the stress strain behaviour of a three block copolymer with 17 weight % styrene and 90 % cis - 1,4 units in the polyisoprene middle block. In fig. 4. the stress strain curves are shown for 3 different temperatures. With decreasing temperature the modulus increases in a similar manner as it has been observed for natural rubber (TRELOAR). This behaviour is typical for crystallization occuring during stretching. Further investigations are being carried out to study the crystallization behaviour of crystallizable styrene-isoprene-styrene block copolymers particulary under the aspect of the influence of block length and morphology.

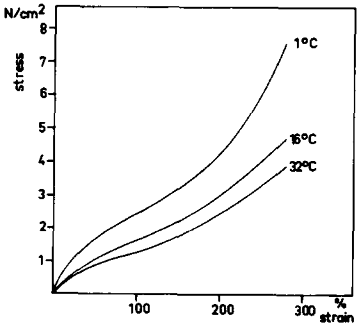

Figure 4:

Stress - strain curves for poly(styrene-b-isoprene-b-styrene), 17 weight % styrene, 90 % cis-1,4 isoprene units in isoprene block, strain rate: 5 mm/min

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Received February 29, 198o
Accepted March 5, 198o