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Polymerization Mechanisms

Living Polymerization

1. Solvent Effect on the Stereoregularity of Polyisoprene Initiated by n-Buthyllithium

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SUMMARY

Isoprene was polymerized using very low concentration of n-Butyllithium in bulk and in different hydrocarbon and polar solvents. The concentration of n-Bu-lithium was kept constant to correlate the influence of solvent on the stereoregularity of the resulting polyisoprene.

INTRODUCTION

It is well known that isoprene can polymerize in four modes i.e. cis-1,4-, trans-1,4- 1,2- and 3,4-structures. However, the properties of polyisoprene as an analogue to natural rubber (Hevea) depend on the proportion of cis-1,4-isomeric structure.

Since it was recognized that lithium can give a very high cis-1,4-polyisoprene (STAVELY et al. 1956), a great deal of work was done concerning the factors affecting the stereoregularity of polyisoprene and some other 1,3-dienes during polymerization. The influence of the nature of solvent on the microstructure of organolithium initiated polyisoprene was discussed in two recent excellent review articles (MORTON 1983, YOUNG et al. 1984). However, in most ot the work discussed, the content of different polyisoprene isomers were not consistant. This could well be due to the variation in the initiator concentrations and polymerization temperature.

In this work, equal amount of n-Buli (5×10^{-6}mol l^{-1}) were used to initiate the polymerization of isoprene in n-heptane, cyclohexane, n-hexane, benzene, toluene, diethylether (DEET), 2-methyltetrahydrofuran(MTHF), oxepane and tetrahydrofuran (THF) at 25°C.

EXPERIMENTAL

The methods employed for purification of solvents, dilution of n-Buli and purification of isoprene were similar to those reported earlier (AL-JARRAH 1978). Furthermore, the polymerization reactor was purged with living polystyryllithium solution before solvents (if used), dried over sodium-potassium alloy, were distilled from their living polymer solution to the reactor. Isoprene, purified by distillation from dibutyl magnesium, was introduced to the reactor from graduated tube. n-Buli (15 wt% in n-hexane) was carefully diluted with dry n-hexane to the desired concentration using dilution apparatus. The apparatus was equipped with twelve ampoules connected through two side arms to a 250 ml round bottom flask (AL-JARRAH 1978). The required amount of 2M n-Buli solution was introduced to the dilution apparatus by hypodermic syringe under nitrogen. The amount of n-hexane, needed to reduce the concentration of n-Buli in each ampoule to 5×10^{-6} mol l^{-1} was distilled from graduated tube. The concentration of n-Buli was determined by the double titration method (GILMAN and CURTLEDGE 1964).

Polymerization reaction,carried out at 25°C, was initiated by opening the ampoules containing n-Buli into the reactor containing isoprene with or without solvents.
After 24 hr the living polymer solutions were terminated with degassed methanol. Polyisoprenes were precipitated in methanol and dried to constant weight under vacuum.

The exact amounts of polyisoprene isomers were determined from their ^{1}H-NMR and ^{13}C-NMR spectra which were recorded on a Varian FT 80 A spectrometer equipped with a fourier transform accessory.

The amounts of 3,4 and 1,4 isomers were determined from their ^{1}H-NMR spectra in CCl_4 solution, using TMS as an internal standard. The signals at 5.08 and 4.68 ppm correspond to 1,4 and 3,4 units, respectively (TANAKA et al. 1971). However, the amounts of 1,2 units were calculated from the difference.

The percentages of cis 1,4 and trans 1,4 isomers were determined from the ^{13}C-NMR spectra of 20 % W/V polyisoprene solutions in $CDCl_3$ at 20.0 MHz.

The spectra were proton noise-decoupled and obtained with pulse repetition time of 3.0 sec. The chemical shifts relative to TMS were similar to those reported elsewhere (DUCH et al. 1970). The cis isomer was identified by its signals at 32.25 and 134.85 ppm, whereas the trans isomer was identified by its signals at 39.67 and 134.38 ppm.

RESULTS AND DISCUSSION

The results concerning the n-Buli initiated polymerization of isoprene in bulk and in different solvents at 25°C are shown in Table 1.
In this study, the content of the initiator (n-Buli) was kept constant at very low concentration. Polymerization temperature was also constant (25°C). At such conditions it was possible to obtain a very high cis-1,4 content (98 %) in bulk. This result is a little superior to a recent report using comparable conditions (MORTON and RUPERT 1983). Likewise a higher cis-1,4 content was obtained in heptane, cyclohexane and n-hexane.

TABELE 1

Microstructure of Polyisoprene obtained from Polymerization of Isoprene by n-Buli in Different Solvent at Ambient Temperature (25°C)

System No	Initiator mol $l^{-1}x10^6$	Solvent	1,4-cis	1,4-trans	3,4	1,2
1	5	None	98	-	2	-
2	5	n-Heptane	95	2	3	-
3	4.6	Cyclohexane	92	5	3	-
4	5.3	n-Hexane	90	6	4	-
5	5	Benzene	72	20	8	-
6	5.2	Toluene	68	25	7	-
7	4.8	DEET	2	38	50	10
8	5	MTHF	-	22	58	20
9	5.3	Oxepane	-	20	60	20
10	4.9	THF	-	11	61	28

These findings could be attributed to the low concentration of the initiator as well as to the absence of any terminating impurities. However, this high cis-1,4 content is not contradicting to the mechanism relating the isomerism of the chain end to its rate of propagation (WORSFOLD and BYWATER 1978). This is because according to that theory, the trans-1,4 content should decrease at low initiator concentration, or high monomer concentration. In this work the concentration of the initiator was very low and the monomer concentration was relatively high (0.9 M). Nevertheless, the peculiar sensitivity of polyisoprene to the nature of solvent observed in its kinetic behaviour could as well be due to the complex nature of the C-Li bond in hydrocarbon solvent rather than to the competition between the rates of chain propagation and isomerization only.

The percentage of cis-1,4- content decreases on passing to aromatic solvents, whereas the 3,4 content increases slightly. These findings are similar to those reported recently (MORTON and RUPERT 1983).

In polar solvent, in absence of association, totally different isomers were obtained because polymerization was carried out in a better solvating media. The disappearance of cis-1,4 was accompanied by the formation of side-vinyl units (1,2 and/ or 3,4). The proportions of these vinyl units were related to the ionic character of the living chain ends. Going from DEET to the better solvating media (THF), the 3,4 content increases.

In DEET, where the active centre is expected to be exclusively a tight ion pair with Li cation, little cis-1,4 (2 %) is observed. No cis 1,4 was reported in the polymerization of isoprene under similar conditions (DYBALL et al. 1979), although the percentage of the other isomers were comparable to our results.

In THF, where the propagating active centre is a loose ion-pair, the highest isomer content was the 3,4 (61 %). Also the highest 1,2 content (28 %) was obtained in this solvent.

MTHF and Oxepane gave equal amounts of 1,2 and 3,4 which are in agreement with its comparable solvation power (AL-JARRAH 1978). Because these results are consistent with the polymerization conditions, it is possible to correlate the nature of the propagating active centre with the resulting polyisoprene isomers. The influence of the solvent on the nature of the C-Li bond was evidenced by the increase of viscosity of living polymer solution in hydrocarbon solvents (AL-JARRAH et al. 1979), AL-JARRAH and YOUNG (1980). In such solvents the living chain end could have a covalent bond, whilst in polar solvent it is expected to be of ionic nature. An investigation (in progress) concerning the influence of various amount of different polar co-solvent on the dimeric nature of the polyisoprenyl lithium in n-hexane revealed a direct correlation between the solvation power of the solvent, the degree of association and the isomers content of polyisoprene.

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