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The Effect of Carbon Dioxide on the Alkali-Metal Initiation of Polyisoprene

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ABSTRACT

The structures of polymers formed when alkali metals are placed in the vapor phase above isoprene monomer, both in the presence and absence of carbon dioxide, were investigated. In the absence of carbon dioxide, the polymers were all gel-like and soluble. In the presence of carbon dioxide, however, insoluble popcorn polymers were formed. The structures of the soluble polymers varied from primarily cis in the case of lithium to trans for sodium and potassium initiation. In the presence of carbon dioxide the three alkali metals produced polymers having similar structures, predominantly trans. In the absence of carbon dioxide most of the polymerization proceeds anionically with the majority of the free radical sites of the initially formed radical anion being removed by a transfer reaction or by dianion formation. The presence of carbon dioxide, however, leads to the formation of carboxylate ions that prevent anionic polymerization. Then, due to the structural orientation of the radical anion on the surface, free-radical polymerization occurs, leading to microgelation and popcorn polymerization. This results from cross-linking caused by mechanical rupture of the growing chains.

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INTRODUCTION

Matthews and Strange [1] and Harries [2] discovered in 1911 that sodium acts as a catalyst for the polymerization of isoprene. Holt [3] in 1914 was the first to observe that in the presence of carbon dioxide, a new type of polymer was formed. This polymer was not soluble in organic solvents, oxidized readily in air, and was capable of continued growth when portions (freed from the sodium) were placed into contact with fresh monomer. The characteristics of the polyisoprene initiated by sodium in the presence of carbon dioxide are similar to the popcorn polymers initially encountered in butadiene and GR-S plants [4]. A review of the polymerization data has been presented by Midgley [5] and Whitby [6].

The purpose of the present study was to investigate the microstructures of the polyisoprenes polymerized by alkali metals in the presence of carbon dioxide and to devise a logical mechanism for their initiation and growth.

EXPERIMENTAL

All reactions were carried out in 18 mm diameter glass tubes. The samples of alkali metal were placed on tufts of glass wool approximately 8 cm from the bottom of the tubes. All manipulations were performed in a glove box that was continuously flushed with either nitrogen or argon. After removal from the glove box, the upper portions of the tubes were constricted, the tubes were cooled by immersion in a Dry Ice-acetone bath, and evacuated. Previously dried monomer was then vacuum distilled into the reaction tubes to a depth of approximately 2 to 3 cm, the tubes were flushed by further evacuation, and then sealed. For the experiments in which carbon dioxide was added, the evacuated tubes were opened to an atmosphere of carbon dioxide (from a subliming Dry-Ice source) before being sealed. Polymerizations were then carried out in the vapor phase in the darkness of an oil bath maintained at 60°C.

The isoprene used was 99%+ reagent obtained from Aldrich Chemical Co. The alkali metals were supplied by Matheson, Coleman, and Bell. The lithium was in the form of wire, the sodium as spheres, and the potassium as sticks; all were immersed in oil. Before use, the metals were freed of oil, cleaned, and cut into small sections to expose more surface. All handling of the metals was done under an atmosphere of nitrogen in a glove box. Due to this exposure to nitrogen, subsequent formation of nitrides, especially with the lithium, could occur. Some identical experiments were made with lithium as the initiator in which all manipulations were performed in an atmosphere of argon, but, since no difference was noted in the results of the nitrogen and argon experiments, the majority of the experiments were done under a nitrogen atmosphere.

Following polymerization the tubes were broken open and the polymers were washed with absolute ethyl alcohol to remove the alkali metals. The samples were then either placed in a vacuum or flushed with a stream of dry helium for the removal of volatiles. In order to obtain samples of the popcorn polymers for analysis, the polymers were oxidized for 30 h in the apparatus and manner previously described [7]. The oxidized polymer was then flushed with dry helium for 48 h and the soluble portion removed by dissolving in deuterated chloroform. Only by oxidizing the popcorn polymers could low concentrations of soluble polymer be obtained for analysis.

NMR spectra were obtained on a Nicolet NC-300 instrument. Integrations were made by the paper-weighing technique and checked by electronic integrations.

EXPERIMENTAL RESULTS

Only soluble polymers were obtained when the alkali metals were allowed to react with isoprene in the vapor phase. The lithium-initiated polymer was a light-gray to clear gelatinous mass. The bulk of the lithium was not dispersed throughout the polymer. The sodium-initiated polymer was clear and gelatinous with small specks of the original surface contamination layer scattered throughout. The sodium metal remained intact as a bright, lusterous, metallic mass. The potassium-initiated polymer was clear but contained some cloudy-red material. The potassium metal was not dispersed and was coated with a dark-red substance.

In contrast to the gelatinous polymers that resulted from the alkali-metal initiations, the polyisoprenes produced under the same experimental conditions, but in the presence of carbon dioxide, were all highly cross-linked insoluble polymers. In all cases the alkali metal did not remain intact, but was uniformly dispersed throughout the polymer. Popcorn polymer formation was complete for the potassium-carbon dioxide initiated polymerization after 4 d at 60°. The sodium-carbon dioxide system required 5 to 6 d, and for lithium-carbon dioxide approximately 19 d were required for complete popcorn formation.

The lithium-carbon dioxide polymer was white with relatively large pieces of lithium dispersed throughout. The sodium-carbon dioxide polymer was gray with the sodium uniformly dispersed throughout; it had the appearance of a brainlike structure. The potassium in the potassium-carbon dioxide polymer was also dispersed throughout the reddish-tan colored mass, but there were significant portions of white popcorn containing no significant coloration. All the polymers were white in color after treatment with alcohol to remove the residual alkali metals.

The polyisoprenes initiated in the presence of carbon dioxide all had the ability to propagate when reseeded above fresh monomer. The typical popcorn growth rate for a sodium-carbon dioxide polymer is shown in Fig. 1.

The microstructure of free-radical initiated polyisoprene popcorn

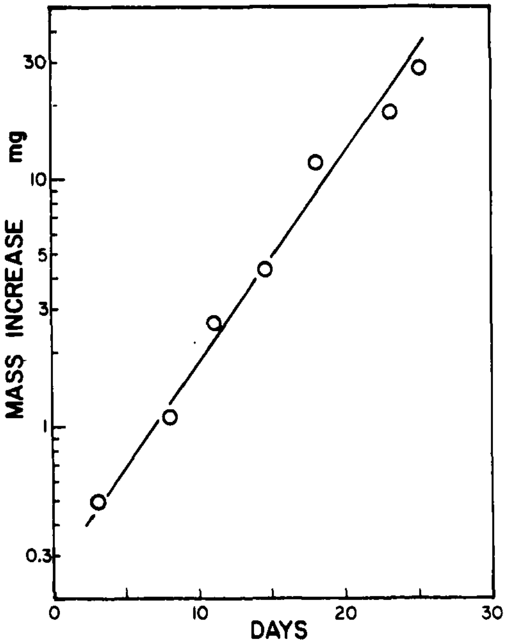


FIG. 1. Growth of sodium-carbon dioxide initiated polyisoprene popcorn polymer.

polymer has recently been investigated by NMR techniques [7]. In order to obtain the spectra, the soluble portion of partially oxidized polymer was used for analysis. The same technique was used in the present work. It should be noted that there is no cis-trans isomerization during the thermal oxidation of polyisoprene [8].

A typical NMR spectrum, that for the lithium-carbon dioxide initiated polyisoprene popcorn polymer, is shown in Fig. 2. The assignments for the resonance peaks have been discussed [7], but it should be pointed out that the polymer has been oxidized and resonances due to oxidation, such as the 1.31 $(\mathrm{CH{-}\overset{|}{\underset{|}{C}}{-}O{-}})$ ppm peak, are prominent parts of the spectrum.

The results obtained for the microstructures of the polymers are shown in Table 1. Within experimental error, all the alkali-metal carbon dioxide initiated polymers had the same microstructures: 55-57% trans, 37-39% cis, 2-4% 1,2-addition, and 0.2% 3,4-addition. These structures are identical to the structure of polyisoprene popcorn polymers obtained by free-radical initiation: 57% trans, 40% cis, and 3% 3,4-addition [7].

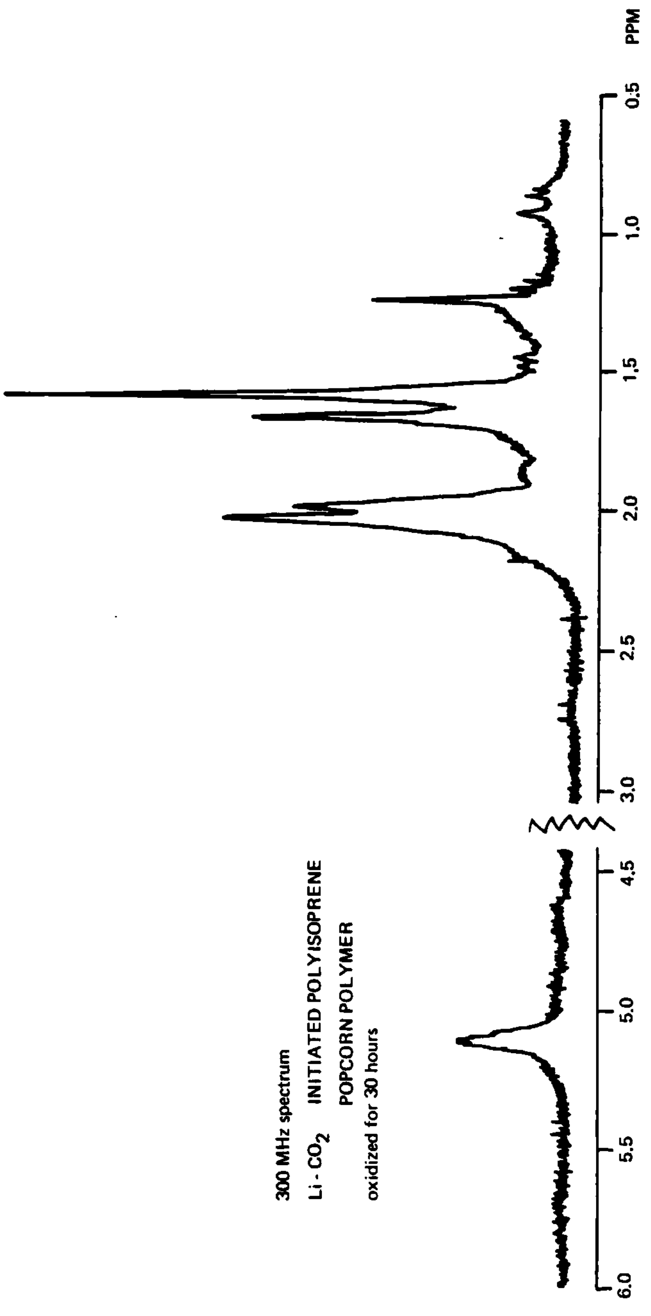

300 MHz spectrum
Li - CO$_2$ INITIATED POLYISOPRENE
POPCORN POLYMER
oxidized for 30 hours
6.0
5.5
5.0
4.5
3.0
2.5
2.0
1.5
1.0
0.5
PPM

FIGURE 2.

TABLE 1. Microstructures of Alkali Metal Initiated Polyisoprenes in the Presence and Absence of Carbon Dioxide

	Trans	Cis	1,2-	3,4-	In-chain vinyl
Li	24	70	0	5	1
Li-CO_2	57	39	3	0	0
Na	25	21	7	44	2
Na-CO_2	56	37	2	2	2
K	32	23	6	38	1
K-CO_2	55	39	4	0	2
Free radical	57	40	-	3	-

TABLE 2. Alkali Metal Initiated Polyisoprenes

		Trans	Cis	1,2-	3,4-
Li	Liquid phase, pentane solvent	0	94	0	6
	Vapor phase, no solvent	24	70	0	5
Na	Liquid phase, pentane solvent	43	0	6	51
	Vapor phase, no solvent	25	21	7	44
K	Liquid phase, pentane solvent	52	0	8	40
	Vapor phase, no solvent	32	23	6	38

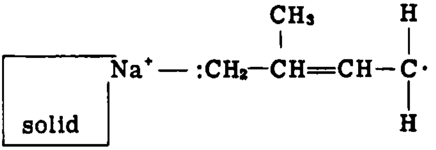
Table 2 gives a comparison of the microstructures of polyisoprenes initiated by alkali metals (no carbon dioxide) in the liquid phase using the nonpolar solvent pentane [9] and those obtained in this work in which the metal was placed in the monomer vapor and no solvent was used. No appreciable change was observed for the 3,4-addition content of the polymers: 5-6% for the lithium and 38-51% for the sodium and potassium. A major difference was observed, however, for the cis-trans contents of the polymers from the two methods of initiation. The liquid-phase work gave 0% trans for the lithium and 0% cis for the sodium and potassium initiated polymers. The vapor-phase initiations produced polymers having the following cis/trans ratios: for lithium, 70/24; for sodium 21/25; for potassium, 23/32.

DISCUSSION

All the experimental data indicate a free-radical mechanism for the alkali metal-carbon dioxide initiated popcorn polymerizations. The structures of the polymers are, within experimental error, identical to polyisoprene popcorn polymers prepared by free-radical methods.

Using the sodium-carbon dioxide system as an example, a tentative mechanism can be formulated for the polymerizations leading to popcorn polymer.

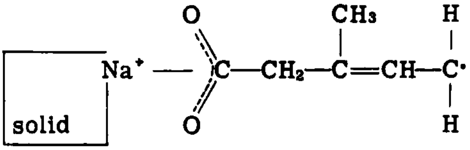
1. The isoprene monomer on contact with the sodium metal forms the expected radical anion by an electron transfer.



$$\boxed{\text{solid}}\,\text{Na}^+ — :\text{CH}_2\text{—}\overset{\text{CH}_3}{\text{CH}}\text{=CH—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\cdot \qquad (1)$$

2. Carbon dioxide then inserts to give the carboxy linkage. This is a fast reaction.

Structure (1) + CO$_2$ →

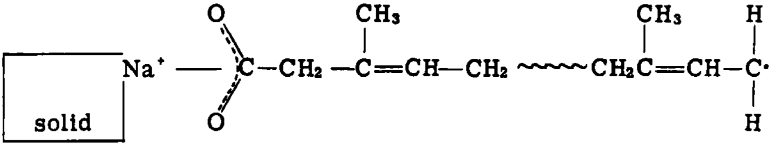


(2)

3. Due to the strong ionic bonding between the sodium ion and the carboxylate ion, and the immobility of the structure, a dianion cannot readily form.

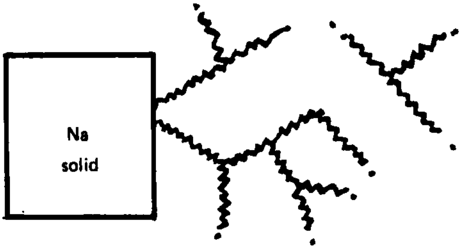
4. Polymerization then occurs via a free-radical mechanism.

Structure (2) + monomer →

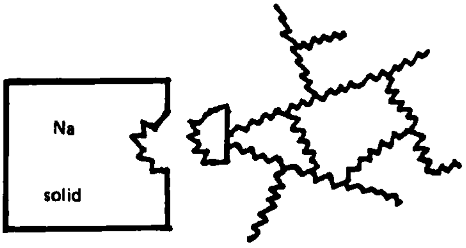


5. The orientation and close proximity of the growing chains attached to the metal surface permits the early onset of microgelation.

6. Growth of the extensively cross-linked polymer causes mechanical rupture of carbon-carbon bonds and leads to the typical popcorn polymerization growth rate that is proportional to the mass of polymer present.

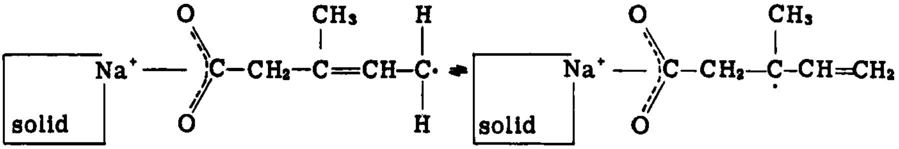


7. The sodium-carboxylate bonds remain intact and the sodium-sodium metallic bonds are broken. This results in the metal being dispersed throughout the polymer mass.



8. The same mechanism prevails regardless of the alkali metal used for the initiation. There is no opportunity for stereoselectivity.

The question of the position of the isoprene methyl groups in the polymer, i.e., is it a 1,4- or a 4,1-addition, was resolved by Morton and Fetters [10] who, for the case of lithium initiation, found the chain ends to be exclusively 4,1- with respect to the metal. From the allylic structure



one might expect a considerable amount of 1,2-addition in the resulting polymers, but only small amounts are formed. This can possibly be explained by the difficulty the incoming monomer has in approaching the ν-carbons due to the tight, rigid packing of the chains attached to the metal surface.

The logarithmic growth rate of popcorn polymers via the mechanical rupture of carbon-carbon bonds has been discussed [11]. The firm attachment of growing polymer chains to a metal with the resultant rupture of the metal structure has been observed by the author in another system [12]. Butadiene popcorn polymerization initiated on the surface of a strip of pure iron (99.9%) resulted in the disruption of the solid metal and its dispersal throughout the polymer mass.

For the soluble polymers initiated by alkali metals alone in the presence of monomer vapor, it is possible that both anionic and free-radical mechanisms are operative. Evidence for this comes from the altered cis-trans ratios. For a purely anionic-initiated polyisoprene in a nonpolar solvent, using lithium, the polymer was 94% cis with no trans structure. The lowering of the cis content to 70% and the appearance of 24% trans would indicate some degree of free-radical propagation. Similarly, the change from 0% cis in the case of the purely anionic polymerization to 21 and 23% cis for the sodium and potassium vapor-phase initiated polymers is undoubtedly due to the occurrence of some free-radical polymerization.

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