

butadiene was found to be 15.72 ± 0.08 . Assuming the process to be



then $A(\text{C}_2\text{H}_3^+) = \Delta H_f(\text{C}_2\text{H}_3^+) + \Delta H_f(\text{C}_2\text{H}_3) - \Delta H_f(1,3\text{-butadiene})$. Using Field's value of $\Delta H_f(\text{C}_2\text{H}_3) = 82$ kcal./mole,¹⁸ this appearance poten-

(18) F. H. Field, *J. Chem. Phys.*, **21**, 1506 (1953).

tial gives $\Delta H_f(\text{C}_2\text{H}_3^+) = 307$ kcal./mole, a value considerably higher than the average of 281 kcal./mole obtained by Field from a number of compounds. Evidently this dissociation process involves some 26 kcal. of kinetic or excitational energy.

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[CONTRIBUTION OF THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Isoprene Polymerization by Organometallic Compounds. I

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Organometallic compounds of lithium, sodium and potassium were used to initiate the polymerization of isoprene in various solvents. The effects of temperature, solvent, organic moiety and metallic ion on the structure of the polymer are reported. The controlling factors are the solvent and the nature of the positive counterion. For example, with *n*-butyllithium and heptane, over 90% *cis*-1,4-structure is obtained; with *n*-butyllithium or phenyllithium in tetrahydrofuran practically no 1,4-structure appears in the polymer; sodium and potassium compounds give quite different structures.

Introduction

In a previous publication (Hsieh and Tobolsky¹) it was shown that in hydrocarbon solutions (benzene or heptane) of isoprene, *n*-butyllithium produced a polymer which had more than 90% *cis*-1,4-structure. In diethyl ether solutions of isoprene, butyllithium produced a polymer which had approximately 60% 3,4-structure, 10% 1,2-structure and 30% *trans*-1,4-structure. The most striking difference between these polymerizations was that under our conditions a precipitate was always present during the polymerization in hydrocarbon solutions, while the ether solutions appeared homogeneous during polymerization and showed little or no Tyndall effect. This work in no way proves that stereospecific polymerization could not occur under homogeneous conditions, but it did not in our experiments.

In this present work isoprene was polymerized by various organometallic compounds and in various solvents mostly under homogeneous conditions. It was our desire to evaluate the effect of temperature, solvent, organic moiety and positive counterion on the structure of the polymer.

Experimental

Material.—The organometallic compounds were synthesized and analyzed according to the procedure described by Gilman.² Phillips 99 mole % isoprene was redistilled under nitrogen before use. The solvents were carefully purified by well-known methods.

Polymerization.—The polyisoprenes were prepared by the evacuated sealed tube technique or in 2-ounce bottles with caps having self-sealing gaskets through which the reagents were injected by means of syringe needles. Manipulations with the reagents were conducted in a dry box and in an atmosphere of purified nitrogen.

The concentration of the catalysts used was 1 mole % with respect to the weight of isoprene. The volume of the solvent was 2.5 times that of the monomer. Polymerizations were allowed to proceed to at least 80% conversion. Light scattering properties of the reaction mixtures strongly suggested homogeneous polymerization. However, as polymerization approached 100% conversion, the reaction mixture darkened markedly so that possible Tyndall effects were obscured.

(1) H. Hsieh and A. V. Tobolsky, *J. Polymer Sci.*, **25**, 245 (1957).

(2) H. Gilman, *et al.*, *THIS JOURNAL*, **64**, 1957 (1932); **62**, 1514 (1940).

The polymers were isolated by slowly pouring the reaction mixture into methanol containing α -naphthylamine. Purifications were undertaken by repeated solution in benzene and precipitation with methanol. The purified polyisoprenes finally were dried *in vacuo* and 1% carbon disulfide solutions were prepared and studied by spectral analysis as described by Richardson.³ The percentages of 1,2 *versus* 3,4- and 1,4-structures are probably valid within 3%; the relative amount of *cis*-1,4 *versus trans*-1,4 is valid to about 10%. The polymers ranged from sticky semi-liquids to rubbery solids. Viscosity measurements of the toluene solutions gave molecular weights of from 2000 to 15,000 according to published equations relating intrinsic viscosity and molecular weight.⁴

Results and Discussion

Anionic polymerizations (in homogeneous media) proceed by the following steps. First, the anionic initiator MR dissociates into M^+ and R^- . The anionic moiety R^- adds to the monomer (isoprene) to start a growing polymer chain. The propagating end of the chain is the ion pair (\sim -isoprene $^-M^+$). It is this ion pair that determines the structure of the polymer, because obviously the entering monomer is strongly influenced by the electrical and steric forces of the ion pair as it insinuates itself between the isoprene $^-$ and the M^+ .

Inasmuch as the solvent may thoroughly solvate or even complex one or both members of the ion pair, one might expect that both the positive counterion and the solvent would have a very important influence on the structure of the polymer in homogeneous systems.

On the other hand, one should expect that the initiating moiety R^- would have much less influence on the structure of the polymer formed in homogeneous systems. Similarly, one might anticipate that the influence of temperature should not be major: higher temperatures might favor a somewhat more random structure.

The extent to which these predictions are borne out is shown in the tables.

Table I shows the major effects produced in the structure when the positive counterion and the solvent are varied. Column 1 gives the initiator; column 2 gives the solvent; column 3, the temper-

(3) A. Richardson and W. Sacher, *J. Polymer Sci.*, **14**, 353 (1953).

(4) W. C. Carter, R. L. Scott and M. Magat, *THIS JOURNAL*, **66**, 1840 (1946).

TABLE I

Initiator	Solvent	T, °C.	Nature of system	Structure, %			
				1,2	3,4	<i>trans</i> -1,4	<i>cis</i> -1,4
<i>n</i> -Butyllithium (see ref. 1 and 5)	Heptane	42	Heterogeneous	0	9	0	91
	Benzene	42	Heterogeneous	0	9	0	91
	Ether	30.5	Homogeneous	7	69	24	0
	Tetrahydrofuran	30.5	Homogeneous	31	69	0	0
Phenyllithium	Ether-heptane	25	Homogeneous	3	29	68	0
	Ether	25	Homogeneous	7	61	32	0
	Tetrahydrofuran	25	Homogeneous	33	61	7	0
	Ether-dioxane	25	Homogeneous	25	70	5	0
	N-Dimethylaniline	0	Homogeneous	11	83	6	0
Phenylsodium	Heptane	40	Heterogeneous	10	83	7	0
	Tetrahydrofuran	40	Homogeneous	12	9	79	0
Benzylsodium	Heptane	40	Heterogeneous	12	70	18	0
	Tetrahydrofuran	40	Homogeneous	9	8	83	0
Benzylpotassium	Dioxane	40	Homogeneous	24	60	16	0

ature of polymerization; column 4 states whether the system was homogeneous or heterogeneous and the subsequent columns give the polymer structure. In column 3 the terms heterogeneous or homogeneous merely signify whether a gross precipitate was visible or not: we have no way of knowing whether the polymerizations proceed on the surface when a precipitate was present.

The initiators presented in Table I are *n*-butyllithium, phenyllithium, phenylsodium, benzylsodium and benzylpotassium. The solvents used were heptane, benzene, ether, dioxane, tetrahydrofuran and dimethylaniline. The temperatures were between 0 and 40°.

The most striking structure difference occurred with butyllithium using heptane or benzene as solvent medium. Under our conditions a precipitate formed when isoprene was admitted to these solutions. The polymer formed was over 90% *cis*-1,4. Similar results were obtained using metallic lithium dispersions and other alkylolithiums as shown in a previous publication.⁵ Unfortunately, we were unable to obtain polymer with aryllithiums using benzene or heptane as the solvent. The structures obtained with butyllithium in tetrahydrofuran under homogeneous conditions were quite different from those obtained in heptane or benzene.

Furthermore, the structures obtained with butyllithium in tetrahydrofuran and with phenyllithium in tetrahydrofuran are rather similar, showing the rather minor effect of the organic moiety on structure. This will be further exemplified in later tables. On the other hand, these structures are both very different from that obtained with phenylsodium or benzylsodium in tetrahydrofuran, showing the major effect of the positive counterion. Many more examples of these principles can be adduced from Table I.

The effect of solvent is also shown to be a major one in Table I. Especially interesting is the case of the various solvents studied with phenyllithium. All of these polymerizations proceeded apparently under homogeneous conditions, but there was quite a variation of structure of the polymer made in these solvents. (In the case of mixed solvents we used equal volumes of each.)

(5) H. Hsieh, D. J. Kelley and A. V. Tobolsky, *J. Polymer Sci.* (in press).

Even greater differences were obtained with the same initiator if in one case the polymerization occurred in a solvent which gave a homogeneous polymerization and in the other case the polymerization occurred in a solvent which gave heterogeneous polymerization. This has been discussed already for butyllithium, but it is also true for phenylsodium and benzylsodium. The difference in structure may well be due to the fact that the polymerization in the heterogeneous systems is occurring on the surface, and the surface is acting as a gigantic counterion of a very special nature. On the other hand, we may be witnessing in these cases extreme examples of a solvent effect. Though the former seems more likely, we cannot exclude completely the latter as a possible explanation. The well known formation of micelles by lithium alkyls in non-polar solvents may certainly have a profound influence on the phenomenology of these reactions, even in apparently clear solutions. The fundamental question is: must the all-*cis* structures arise from a qualitatively different mechanism than the other structures.

Ideally, it would have been best if all the data shown in Table I were obtained at the same temperature. Because the rates might be too fast or too slow for some of the initiators if we used a single temperature, we were compelled to use several temperatures. However, the effect of temperature on structure is not exceedingly large. This is shown in Table II, where the structures of

TABLE II
EFFECT OF TEMPERATURE ON ISOPRENE POLYMERIZATION
INITIATED BY PHENYLLITHIUM IN TETRAHYDROFURAN

Temp., °C.	Structure of polymer, %			
	1,2	3,4	<i>trans</i> -1,4	<i>cis</i> -1,4
-78	30	63	7	..
0	32	62	6	..
25	33	61	6	..
38	33	61	6	..
100	35	57	8	..

the polymer produced with phenyllithium in tetrahydrofuran are shown. Here the variation of structure between -78 and 100° is very small. On the other hand, somewhat more variation of structure with temperature is shown for phenyllithium-ether in Table III.

TABLE III
EFFECT OF TEMPERATURE ON ISOPRENE POLYMERIZATION
INITIATED BY PHENYLITHIUM IN ETHER

Temp., °C.	Structure of polymer, %			
	1,2	3,4	<i>trans</i> -1,4	<i>cis</i> -1,4
-78	9	69	22	..
0	9	68	23	..
25	7	61	32	..
38	5	47	48	..

In Table IV the structure of various aryllithium initiated polyisoprenes is shown. The data are quite definite in showing a very minor effect on structure as produced by different organic anions.

TABLE IV
STRUCTURE OF ARYLLITHIUM INITIATED POLYISOPRENES

Aryl group	Solvent	Temp., °C.	Polymer structure, %		
			1,2	3,4	1,4 (<i>trans</i>)
<i>p</i> -Tolyl	Ether	0	6	61	33
<i>p</i> -Tolyl	Ether	25	7	46	47
<i>o</i> -Tolyl	Ether	25	3	65	32
<i>o</i> -Tolyl	Tetrahydrofuran	25	26	69	5
α -Naphthyl	Tetrahydrofuran	25	28	65	7

Finally, it is worth mentioning that in cationic polymerization of isoprene and butadiene, concurrent work going on in this Laboratory shows rela-

tively slight changes of structure with initiator and solvent.⁶ Perhaps the carbonium ion is less affected by its counterion than the carbanion.

In conclusion, we have observed the following results using organometallic initiators in isoprene polymerization. These are consistent with the anionic mechanism.

1. Extremely large variations in structure with changing positive counter ion in homogeneous solutions.

2. Extremely large differences in structure in certain cases depending on whether the reaction is homogeneous or heterogeneous. Perhaps the surface is to be regarded as a large counterion of a special nature. On the other hand, we may here have an extreme case of a solvent effect.

3. Large effects of solvent on the structure of the polymer produced in homogeneous solution. The solvent can certainly influence the electrical forces between the components of the ion-pair.

4. Very small effect of temperature in one solvent; a fairly important effect of temperature in another.

5. Relatively small effect of negative ion (the organic moiety).

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(6) T. Ferington and A. V. Tobolsky (in preparation).

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Kinetics and Mechanism of the Reactions between Chloroquoquochromium(III) Ions and Silver Ion

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The reaction of the dichlorotetraquoquochromium(III) ion with Ag(I) was studied in high hydrogen ion activity (3 to 6 *M* perchloric acid) so that the contributions due to basic and polymeric species were negligible; the only ligands available for complexing chromium were chloride ions and solvent water. Rates were followed by titrimetric determination of Ag(I) concentration; reaction products in terms of chromium species were verified by spectra. The reaction consists of two well-defined steps: conversion of the dichlorotetraquo ion to chloropentaquoquochromium(III) ion and AgCl, followed by conversion of the chloropentaquo ion to the hexaquo species. Rates for both reactions are second order, proportional to both Ag(I) and Cr(III) concentrations; rate constants in 6.0 *M* perchloric acid at 25° are 132 ± 45 l. mole⁻¹ hr.⁻¹ for the first reaction and 0.41 ± 0.01 l. mole⁻¹ hr.⁻¹ for the second. The rates increase with decrease in perchloric acid concentration. The energy of activation for the second reaction in 3 *M* perchloric acid is 25 kcal./mole; the entropy of activation is +1.6 e.u. The aquation rate of the dichlorotetraquoquochromium(III) ion is many times as rapid in the presence of silver as in its absence. The kinetics indicate a reaction mechanism involving formation of a chloride bridge between Cr(III) and Ag(I); this is then followed by the loss of silver chloride and the addition of the water to the residual pentacoordinate chromium species.

The classic establishment of the formulas of the differently colored isomeric chromic chloride hydrates which provided one of the foundations for Werner's theory of coordination compounds and our contemporary views on inorganic complex species, was largely based upon the evidence presented by the reaction of these salts in aqueous solution with Ag(I). The salts were shown to be the violet $[\text{Cr}(\text{H}_2\text{O})_6]^{+3}$, the light green $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{+2}$ and the dark green $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$. However, in titration of their chlorides with silver, many investigators reported precipitation of varying amounts of chloride ion in excess of that predicted by Werner's coordination theory. Such discrepancy was as-

cribed to chloride produced by dissociation of the complex during titration.

Meanwhile, data, accumulated on the rates of interconversion of the three Cr(III) species, indicated (a) a very slow aquation (replacement of ligand Cl by H₂O), (b) the strong *pH*-dependence of the process (inhibition by increasing hydrogen ion concentration), and (c) the reversible formation of hydroxo and polynuclear species on aging a Cr(III) solution. The rates of exchange of solvent H₂O and Cl⁻ with complexed H₂O and Cl⁻ were shown to be very slow. The slow rates of equilibration permit the first three members of the series to be separated from non-equilibrium mixtures as crystalline chlo-