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Molecular Structure of Conjunct Polymers

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Conjunct polymers are incidental by-products of acid-catalyzed hydrocarbon reactions. The structures of these oils were determined with the aid of physical property correlations, ultraviolet, infrared, and mass spectroscopy, and various chemical methods, including hydrogenation. The conjunct polymers were thus shown to be cyclic polyolefinic hydrocarbons with a high proportion of conjugated double bonds, no two of which are in the same ring ("heteroannular conjugation'). Five-membered ring systems predominate, but larger, and possibly also smaller, rings are believed to be present. Both condensed and uncondensed ring systems are assumed. An average molecule may be considered to be dicyclic, with one pair of conjugated double bonds and one-half to one and one-half isolated double bonds. About 60% of the carbon atoms are in side chains. Polymer distillate fractions with as many as five rings and four double bonds per mole have been observed.

CONJUNCT polymers are highly olefinic oils which are produced by acid-catalyzed reactions of hydrocarbons. Under the proper conditions they may be formed from any type of hydrocarbon except aromatics. The nature of the acid is not critical. Usually, however, the catalyst involved is hydrofluoric acid, sulfuric acid, phosphoric acid, boron trifluoride, aluminum chloride, or combinations of these.

As a rule, the conjunct polymer is an undesired by-product of some other reaction, such as alkylation, polymerization, or isomerization. The polymer forms a complex with the catalyst. It is liberated by neutralization or hydrolysis of the catalyst phase, and appears as a light yellow to dark red oil with a characteristic odor. It is also commonly referred to as "red oil," "sludge," or "acid oil."

Conjunct polymers are exceedingly complex mixtures of highly olefinic, conjugated cyclic hydrocarbons. Ipatieff and Grosse (*14*) first recognized that these materials are polymeric in nature. They also realized that the process of forming them is different from conventional polymerization, since it involves such additional reactions as hydrogen transfer and cyclization, and the starting material is not necessarily olefinic. They employed the term "conjunct polymerization" to define this combination of reactions. Since then, many workers have used the term "conjunct polymer" to refer to the polyolefinic oil produced in acid-catalyzed reactions of hydrocarbons.

The technical literature on conjunct polymers is largely concerned with utilization. It is, therefore, restricted mainly to patents, only a few of which are pertinent to the work described in this article (*3, 12, 15, 16, 19, 20, 21, 29*). Apparently the only reported studies on the analysis of these oils are by Bloch and his associates (*2, 3, 12, 15, 29*). On the basis of ultraviolet and infrared spectra and certain other properties, they concluded that the conjunct polymers are five-membered ring hydrocarbons with from two to over four double bonds per mole, two of which are conjugated. They also reached the significant conclusion that the conjugated double bonds are probably distributed between a ring and a side chain, and that the polymers have a high degree of alkyl and/or alkenyl substitutions.

Workers in this field undoubtedly realized that conjunct

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Table I. Preparation and Recovery of Conjunct Polymers

Polymer	Catalyst	Hydrocarbon Charge	Type of System	Catalyst to Hydrocarbon Ratio (Wt.)	Temp., ° F.	Pressure, P.S.I.G.	Space Velocity, V./Hr./V.
I	Anhydrous HF	Dearomatized virgin gas oil	Flow	1.0	355	1500	3.5
II	Anhydrous HF	95 mole % isobutene	Batch stirring reactor	0.4	212	Above atmospheric	[a]
III	Anhydrous HF	Butane-butene stream (42% olefins) from catalytic cracking unit	Flow	0.2–2.2	200–280	350–600	1.0–4.0
IV	Anhydrous HF	Butane-butene stream (42% olefins) from catalytic cracking unit	Flow	0.2–2.2	200–280	350–600	1.0–4.0
V	98% H_2SO_4	Isobutane-butene mixture	Kellogg sulfuric acid alkylation unit	2–3	35–45	4–9	[b]
VI	98% H_2SO_4	Isobutane-butene mixture	Stratco sulfuric acid alkylation unit	2–3	40–50	30–40	[c]
VII	$AlCl_3$ (plus 2% H_2O)	2,2,4-Trimethylpentane	Batch	0.5	140–176	15	. . .

Methods of Recovery of Polymers

I	1. Cold settling 2. Separation of HF phase 3. Heating to 115° F. to strip 85–90% of HF 4. Neutralization of remaining HF with aqueous KOH solution.
II	1. Cold settling 2. Neutralization of acid layer with concentrated NH_4OH.
III	1. Cold settling 2. Flashing off of excess HF to about a 60% HF–40% oil solution 3. Neutralization of solution with aqueous KOH.
IV	1. Cold settling 2. Flashing off of excess HF to about a 60% HF–40% oil solution 3. Dilution with aqueous HF of approximately azeotropic composition and addition of heptane, in decanter system 4. Separation of heptane solution and stripping of heptane.
V	1. Dilution of acid with water and ice 2. Extraction of hydrolyzate with *n*-heptane 3. Washing of heptane solution with aqueous KOH and water 4. Stripping of heptane.
VI	1. Dilution with ice and water 2. Extraction of hydrolyzate with *n*-hexane 3. Caustic and water-wash of extract 4. Drying of extract 5. Stripping with nitrogen in steam bath.
VII	1. Separation of $AlCl_3$ complex layer 2. Hydrolysis of complex in ice-water mixture 3. Water wash of polymer layer.

[a] Contact time 30 minutes. [b] Contact time 15–40 minutes. [c] Contact time approximately 30 minutes.

polymers are complex mixtures with a wide boiling range. The past emphasis on the monocyclic portions of these oils has been an attempt to simplify the presentation of their structures. In this laboratory, on the other hand, most of the conjunct polymers encountered had only a small percentage of monocyclic molecules. In fact, some of them contained fractions with as many as five rings per mole. Any attempt to represent the typical molecules present in these oils as monocyclic compounds would be an oversimplification.

Conjunct polymers are usually side products of many commercially important processes, particularly in the petroleum industry. The reaction mechanisms of all these processes have not been completely explained. Neither is the effect of conjunct polymerization on the course and final products of these reactions entirely understood. A more thorough knowledge of the structures present in these oils should be helpful in defining their role. Consequently, a systematic study of the structures present in conjunct polymers was undertaken, using as the basis an analytical method previously reported from this laboratory (*26*).

EXPERIMENTAL

Conjunct Polymers Studied. The polymers reported in this study were derived from hydrocarbon reactions catalyzed by hydrofluoric acid, sulfuric acid, and aluminum chloride. The most intensive analysis was made on polymer I, which was the by-product of a reaction involving the cracking of dearomatized gas oil in the presence of anhydrous hydrofluoric acid at 355° F. Polymers II, III, and IV were obtained from hydrofluoric acid-catalyzed reactions involving olefinic charge stocks. Polymers V and VI were obtained from the spent sulfuric acid of commercial isobutane-butene alkylation units of two different designs. Polymer VII was prepared in the laboratory by the aluminum chloride-catalyzed reaction of a branched paraffin.

The complete characterization scheme was carried out only on polymers I through V. Polymers VI and VII have essentially similar properties and are included for comparison purposes.

The detailed conditions of preparation and recovery of the seven polymers described in this study are summarized in Table I. Their properties are shown in Table II. Polymers V and VI contained higher contents of oxygen, sulfur, and ash than the other polymers. For this reason, the data derived from polymer V (and, by inference, from polymer VI) may be less accurate than those from the other polymers. The conclusions, however, are considered to be well within the boundaries of experimental error.

Hydrogenation. One of the required steps in the basic analytical scheme (*26*) is hydrogenation. A preliminary decision must be made as to whether the hydrogenation should be carried out selectively or nonselectively. Selective hydrogenation is generally more time-consuming, but is necessary if the material is known or suspected to contain both olefinic and aromatic double bonds.

The ultraviolet absorption spectrum may be used to decide whether or not selective hydrogenation should be employed. Strong general absorption, or absorption bands, at about 250 mμ and higher generally indicate aromatic structures (*26*). However, this criterion must be applied with caution, as it is shown below that certain conjugated olefinic types also absorb in this general region. Consequently, polymer I, which has a strong absorption band at approximately 249 mμ, was hydrogenated selectively as a test case. The complete lack of ultraviolet absorption which was found after no further hydrogenation occurred under selective conditions confirmed the absence of aromaticity. To save time, the other polymers, none of which showed absorption bands above 250 mμ, were hydrogenated nonselectively.

For polymers II, III, IV, and V the hydrogenations were carried out in an American Instrument Co. superpressure rocking autoclave at 150° to 225° C. and 1500 to 2500 p.s.i.g. of hydrogen, using 30 weight % of finely divided nickel-on-kieselguhr catalyst. Polymer I was hydrogenated with 0.5 weight % of Raney nickel catalyst at 115° to 120° C. and 1500 to 2100 p.s.i.g. of hydrogen in a Monel stirring autoclave. In all cases the hydrogenation was discontinued after the specific dispersion was reduced to 100 or less and/or negligible bromine numbers were obtained. Usually this required several repeated hydrogenations with fresh batches of catalyst.

Properties of the hydrogenated oils are shown in Table III, along with the structural details computed from these properties. The methods of carrying out these computations (*26*) include correlations for estimating the extent of ring condensation, which are valid only for a limited number of cases. Suitable criteria are described to determine whether or not these correlations are applicable; if inapplicable, the assumption of "50% condensation" is made. It was found by means of these criteria that the extent of ring condensation could not be determined for the hydrogenated conjunct polymers. Therefore, the assumption of 50% condensation, as defined in the analytical method (*26*), was adopted.

The average ring sizes of the hydrogenated oils were calculated by the Kurtz-Lipkin method (*17, 18, 22*); this is applicable to saturated hydrocarbons containing any ring sizes up to eight carbon atoms. The validity of this method, which may be open to question when applied to highly alkylated materials such as the conjunct polymers, is treated below in the discussion.

The published graphs of the Kurtz-Lipkin method are restricted to five- and six-membered rings, which are the types most commonly encountered. However, the correlations of density, molecular weight, and number of rings per mole for hydrogenated polymers II, III, and IV indicated an average ring size below 5.0. Consequently, the Kurtz-Lipkin graphs were supplemented by a graph of density *vs.* molecular weight for four-membered rings. This graph was constructed by computations from the general molecular volume equation of Kurtz and Lipkin, using averages of condensed and uncondensed ring systems, and excluding "buried" carbon atoms and spiranes. This series of curves, applicable to ring systems containing up to eight rings per mole, may be found elsewhere (*27*).

According to the data of Table III, the average molecule of polymers I through V is approximately dicylic. Polymer II must contain an appreciable percentage of monocyclic molecules, as its average number of rings per mole is below 2.00. Polymer I, by contrast, has an average of 2.65 rings per mole and therefore contains polycyclic molecules. The average ring size of all the polymers approximates that of

Table II. Properties of Conjunct Polymers

Property	Conjunct Polymer Oil						
	HF-Catalyzed Reactions				H_2SO_4-Catalyzed Reactions		$AlCl_3$-catalyzed reaction, polymer VII
	Polymer I	Polymer II	Polymer III	Polymer IV	Polymer V	Polymer VI	
°API (60° F.)	21.2	35.1	28.1	27.5	22.1	...	...
Density, 25° C., computed	0.9195	0.8413	0.8798	0.8831	0.9064	0.9057[a]	0.8787[a]
Refractive index, 25° C.	1.5179	1.4800	1.4984	1.4978	1.5010	1.4967	1.4903
Specific dispersion, 25° C.	130.2	134.0	134.6	132.4	106.4	[b]	...
Bromine No.[c]	188	162	131	157	179	194	187
Iodine No.[d]	437	379	402	419	314	381	393
Maleic anhydride value[e]	354	351	362	299	253	298	322
Molecular weight[f]	265	302	295	302	362	265	285
% carbon, found	88.12	87.00	87.75	87.60	81.58	82.12	86.84
% hydrogen, found	11.29	12.74	12.22	12.30	11.45	11.33	12.38
Total, %C + %H, found	99.41	99.74	99.97	99.90	93.03[g]	93.45[h]	99.22
%C, corrected[i]	88.64	87.23	87.78	87.69	87.69	87.88	87.52
%H, corrected[j]	11.36	12.77	12.22	12.31	12.31	12.12	12.48
Molecular formula	$C_{19.6}H_{29.9}$	$C_{21.9}H_{38.3}$	$C_{21.6}H_{35.8}$	$C_{22.0}H_{36.9}$	$C_{26.4}H_{44.2}$	$C_{19.4}H_{31.9}$	$C_{20.8}H_{35.3}$
Type formula	$C_nH_{2n-9.3}$	$C_nH_{2n-5.5}$	$C_nH_{2n-7.4}$	$C_nH_{2n-7.1}$	$C_nH_{2n-8.6}$	$C_nH_{2n-6.9}$	$C_nH_{2n-6.3}$

[a] By pycnometer. [b] Oil too dark for accurate determination. [c] By Francis method (*8*). [d] By mercuric acetate-catalyzed Wijs method (*13*). [e] Expressed as mg. maleic anhydride reacting with 1 gram material under reflux in toluene solution, determined by back-titration with standard alkali. [f] Ebullioscopic, in benzene (*10, 11, 24*). [g] Contained 1.00% sulfur and 2.35% ash. [h] Contained 2.90% sulfur. [i] Corrected % C = 100(%C)/% C + % H. [j] Corrected % H = 100(%H)/% C + % H.

cyclopentane rings. However, polymers I and V may contain six-membered rings. Polymers II, III, and IV (especially II) also appear likely to contain some rings with less than five carbon atoms. All the polymers, particularly II, are heavily alkylated, with 33 to 74% of their carbon atoms in side chains.

Olefinicity. Bromine and iodine numbers indicate (Table IV) that the conjunct polymers are highly olefinic. These values are only qualitative and cannot be used to compute the true olefinicity. The true double bond content was determined from the increase in hydrogen content after hydrogenation, according to the method of Lipkin, Sankin, and Martin (*23*).

Table IV emphasizes the errors in computing double bond contents from halogen addition values. These errors are expressed as per cent excess double bond indicated. Even partially hydrogenated conjunct polymers give highly erroneous bromine numbers, as much as 200% in error.

On the other hand, type formulas confirm that the double bond contents found by hydrogenation are essentially cor-

Table III. Properties and Structural Composition of Hydrogenated Polymers

Property	Polymer I	Polymer II	Polymer III	Polymer IV	Polymer V
Density, 20° C.[a]	0.9029	0.8323	0.8554	0.8660	0.8673
Refractive index, 20° C.	1.4872	1.4580	1.4670	1.4727	1.4734
Specific dispersion (F-C), 20° C.	99.7	98.3	97.5	101.9[b]	96.0
Bromine No.[c]	3.2	0.2	0.7	2.2	0.4
Molecular weight[d]	273	310	302	303	323
Corrected % C[e]	86.67	85.84	86.28	86.43	86.17
Corrected % H[f]	13.33	14.16	13.72	13.57	13.83
Molecular formula	$C_{19.70}H_{36.10}$	$C_{22.16}H_{43.55}$	$C_{21.70}H_{41.11}$	$C_{21.81}H_{40.79}$	$C_{23.17}H_{44.32}$
Type formula	$C_nH_{2n-3.30}$	$C_nH_{2n-0.77}$	$C_nH_{2n-2.29}$	$C_nH_{2n-2.83}$	$C_nH_{2n-2.02}$
Average No. of rings per mole	2.65	1.38	2.14	2.41	2.01
Average ring size, C atoms	5.8	4.4	4.6	4.7	5.7
Average No. of C atoms per ring[g]	5.0	4.1	4.0	4.1	5.0
Average No of C atoms per mole	19.7	22.2	21.7	21.8	23.2
Average No. of ring C atoms per mole	13.3	5.7	8.6	9.9	10.1
Average No. of alkyl C atoms per mole	6.4	16.5	13.1	11.9	13.1
% naphthenic C atoms	67.5	25.7	39.6	45.4	43.6
% alkyl C atoms	32.5	74.3	60.4	54.6	56.4

[a] By pycnometer. [b] This value of specific dispersion indicates that polymer IV may have been not fully hydrogenated. However, difference does not appear great enough to affect conclusions. [c] Francis method (*8*). [d] Ebullioscopic, in benzene. [e] Corrected % C = 100(%C)/% C + % H. [f] Corrected % H = 100(%H)/% C + % H. [g] Assuming 50% condensation.

Table IV. True and Apparent Olefinicity of Conjunct Polymers

	Polymer I	II	III	IV	V
Apparent No. of double bonds per mole					
From bromine No.[a]	3.12	3.06	2.42	2.97	4.05
From iodine No.[b]	4.56	4.51	4.67	4.99	4.48
True No. double bonds per mole[c]	2.98	2.43	2.54	2.18	3.17
Error in double bonds %					
By Br No.[d]	4.5	26	-4.7	36	28
By I No.[d]	53	86	84	129	41
Type formula, computed					
From Br No.	$C_nH_{2n-9.5}$	$C_nH_{2n-6.9}$	$C_nH_{2n-7.1}$	$C_nH_{2n-8.8}$	$C_nH_{2n-10.1}$
From I No.	$C_nH_{2n-12.4}$	$C_nH_{2n-9.8}$	$C_nH_{2n-11.6}$	$C_nH_{2n-12.8}$	$C_nH_{2n-11.0}$
From hydrogenation	$C_nH_{2n-9.3}$	$C_nH_{2n-5.6}$	$C_nH_{2n-7.4}$	$C_nH_{2n-7.2}$	$C_nH_{2n-8.4}$
Type formula, found	$C_nH_{2n-9.3}$	$C_nH_{2n-5.5}$	$C_nH_{2n-7.4}$	$C_nH_{2n-7.1}$	$C_nH_{2n-8.6}$
No. of conjugated double bonds per mole[e]	1.92	2.16	2.18	1.84	1.87
No. of isolated double bonds per mole	1.06	0.27	0.36	0.34	1.30
% conjugation[f]	64.4	89	86	85	59

[a] Apparent No. of double bonds per mole = (Br No. × molecular weight/15,983).
[b] Apparent No. of double bonds per mole = (I No. × molecular weight/25,382).
[c] By hydrogenation (*23*).
[d] % excess double bonds shown.
[e] (MAV × molecular weight/49,030).
[f] (No. of conjugated double bonds/total No. of double bonds) × 100.

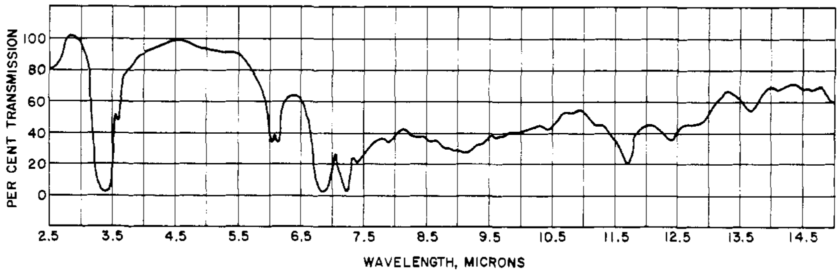

Figure 1. Infrared absorption spectrum of conjunct polymer I

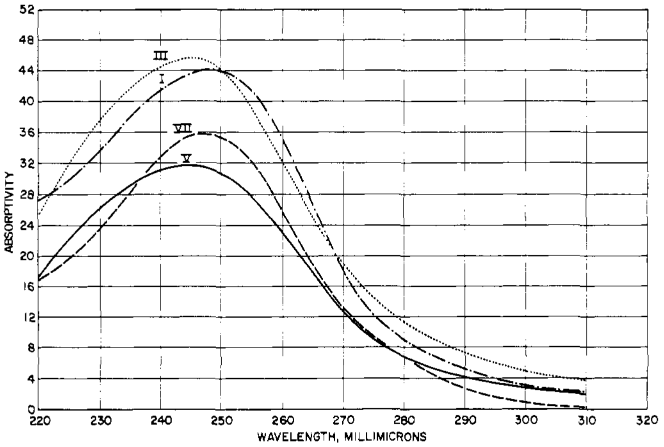

Figure 2. Ultraviolet absorption spectra of typical conjunct polymers

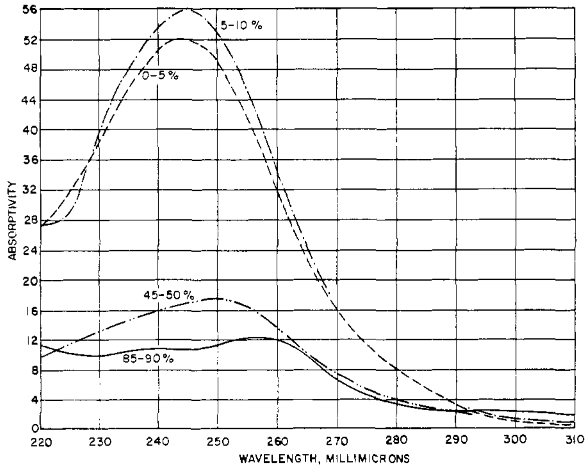

Figure 3. Ultraviolet absorption spectra of distillation fractions from conjunct polymer I

rect. The type formulas of the five polymers are shown in Table IV, computed from the number of rings per mole and the number of double bonds per mole. These computed type formulas are compared with the "found" type formulas, calculated from the percentages of carbon and hydrogen and the molecular weights of the original polymers. The type formulas computed from the double bond contents found by hydrogenation agree well with the found type formulas. On the other hand, the type formulas computed from the double bond contents found by bromine and iodine numbers are grossly in error.

The extent of conjugation of the oils was computed from their maleic anhydride values. A high degree of conjugation is indicated (Table IV). The typical conjunct polymer thus has an average of approximately one pair of conjugated double bonds per mole. In addition, approximately 0.5 to 1.5 isolated double bonds are present in the average molecule.

Infrared Absorption Spectra. Infrared and ultraviolet absorption spectra supplement the basic structures of the conjunct polymers by providing some finer details of structure. The infrared absorption spectra of the conjunct polymers are similar. The spectrum of conjunct polymer I, shown in Figure 1, is an adequate illustration.

The strong absorption bands near 3.4, 6.9, and 7.25 microns are attributed to various types of saturated C-H linkages, the band at 7.25 being specific for methyl groups. Methyl group absorption may be caused by methyl side chains on rings, methyl branches on alkyl side chains, or the terminal methyls on longer alkyl groups. The intensity of absorption of polymer I at 7.25 microns suggests five to seven methyl groups per mole. This agrees well with the 6.4 alkyl carbon atoms per mole (Table III) found by the basic analytical scheme. It also indicates that the saturated side chains in the polymer are small alkyl groups. The absence of normal alkyl groups having more than three carbon atoms in confirmed by the absence of a band near 13.75 microns.

Olefinic bands are seen at 6.04 and 6.15 microns and in the 11- to 15-micron range. The band at 6.04 is characteristic of many aliphatic olefins. The 6.15-micron band may be ascribed to conjugation, although some known cyclopentenes also have a 6.15-micron band. One or more of the bands in the 11.5- to 13.0-micron range taken in conjunction with the 6.04-micron band indicates the presence of tertiary olefins ($R_2C=CHR$), in which R may be either an alkyl group or cycloalkyl residue. The infrared spectrum can neither confirm nor deny the presence of quaternary olefins ($R_2C=CR_2$), as this group has no characteristic absorption in the infrared which would be unique in all cases. However, inasmuch as the absorption bands attributed to the tertiary olefins are only of medium intensity, it seems probable that if the double bonds are highly substituted a preponderance of quaternary olefinic structures should be present.

The absence of significant bands at 11.0 and 11.3 microns rules out terminal olefinic double bonds. Absorption bands at 11.0 microns are specific for unbranched acyclic terminal olefins, such as vinyl groups, whereas bands at 11.3 microns are characteristic of branched terminal olefins—e.g., $R_2C=CH_2$. It also appears unlikely that unsubstituted methylene side chains would be present to any great extent on the rings, as these are related to branched terminal olefins. However, the infrared correlations are less certain for this case.

No alkyne linkages are present in the polymers. This follows from the absence of significant absorption at 4.42 to 4.65 microns. On the other hand, the presence or

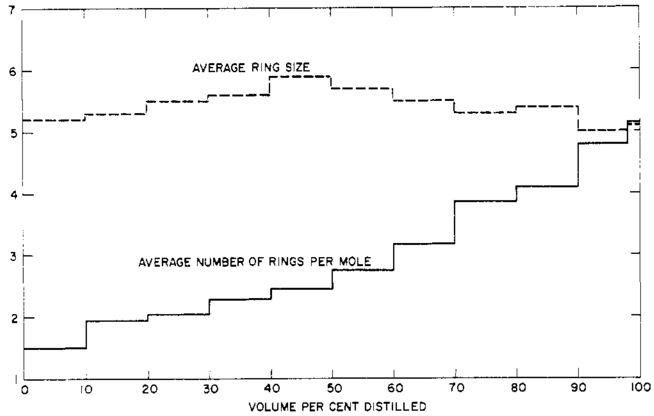

Figure 4. Cyclic features of distillation fractions from hydrogenated polymer I

absence of aromaticity is difficult to determine from the infrared spectrum *per se*; in olefinic oils of this molecular weight range, only a high degree of aromaticity would be unmistakable.

On hydrogenation of polymer I, the longer wavelength bands tend to disappear. When the olefinic bands near 6 microns are eliminated, the partially hydrogenated samples have very low maleic anhydride values, although their total olefinicity is still high. This relates these bands to conjugation in the molecule.

Ultraviolet Absorption Spectra. Probably the single most characteristic property of the conjunct polymers is their ultraviolet absorption spectra, shown in Figure 2 for four of the polymers of Table II. The spectra of the other polymers are similar to these, and overlap them in some cases. These spectra show a single prominent absorption band of high intensity in the 245- to 249-mμ region. The exact position of the absorption maximum may vary somewhat, as illustrated in Figure 3, which shows the ultraviolet absorption spectra of several distillation fractions from polymer I. The progression to higher wavelengths ("bathocromic" shift) shown by the higher-boiling fractions may be explained on a structural basis, as is discussed below.

Hydrogenation of the polymers eventually destroys all ultraviolet absorption between 220 and 310 mμ. However, controlled hydrogenation first eliminates the absorption band in the 245-mμ region. The elimination of this band coincides with the reduction of the maleic anhydride value to zero and thus identifies this band with a conjugated structure.

Absorption bands in the 230- to 250-mμ region have been attributed to conjugation in the case of such cyclic compounds as resin acids (*6*), steroids (*1, 6, 7, 30*), terpinoids (*9, 30*), and certain hydrocarbons (*5, 30*). Moreover, it has been shown that the two double bonds of the conjugated pair are not in the same ring; for if both double bonds are in the same ring the absorption occurs at a much higher wavelength—namely, between 255 and 290mμ (*1, 5, 6, 7, 9, 30*).

Fieser and Fieser (*7*) applied the term "homoannular" to conjugated diene systems with both double bonds in the same ring, and "heteroannular" to conjugated dienes with the double bond pair distributed between two rings. The conjugation existing in conjunct polymers is thus of the heteroannular type. This term is broadened to include systems in which the conjugated pair is distributed between a ring and a side chain, as in the monocyclic fractions of the conjunct polymers.

From data on steroids, Woodward (*30*) developed a set of empirical rules for predicting the absorption maximum of a cyclic diene. According to these rules, assumed to be applicable to conjunct polymers, the unsubstituted diene chromophore absorbs at 217 mμ. Each alkyl substituent or ring residue linked directly to the diene chromophore shifts the absorption maximum 5 mμ in the direction of longer wavelengths. Likewise, each exocyclic double bond—for example, the $=CR_2$ directly attached to a ring—enhances the maximum by 5 mμ, and the effect is twice as great if the same double bond is exocyclic to two rings. The probable structures of typical molecules in the conjunct polymers agree well with these rules. They also help to explain variations in the positions of the absorption bands in the distillation fractions from polymer I.

Detailed Analysis of HF Conjunct Polymer. The conjunct polymers generally have a fairly wide boiling range; for polymer I the initial boiling point is 69° C., and the boiling point at 90% overhead is 236° C., both values being at 25-mm. pressure. The structures derived from the examination of the whole oils are, therefore, bound to be average structures of the many molecules present. To study the distribution of the various structural systems in these oils, it is necessary to examine fractions obtained by some process which separates by molecular size, such as distillation. An analysis of this type was carried out on hydrogenated polymer I.

Distillation of hydrogenated polymer I was begun at atmospheric pressure (764 mm.) through a 15-tray Oldershaw column at 10 to 1 reflux ratio. A 250-ml. charge was used and 25-ml. fractions of overhead were collected. At the end of the third fraction, the pressure was reduced to 100 mm. The distillation was halted at the end of the fourth fraction and the Oldershaw column was replaced with a simple Claisen head. A stream of nitrogen was introduced into the liquid through a minute capillary, and rapid distillation was resumed at 10-mm. pressure. The pot temperatures were generally between 200° and 300° C. throughout the distillation, and never exceeded 345° C. The distillation was carried to the point of 98 volume % overhead, fraction 10 comprising 20 ml.

All the overhead fractions were pale yellow oils, while the 2% bottoms was an amber-colored solid with a grease-like appearance. The four fractions through the 40 volume % range had a terpenic odor, but all subsequent fractions were odorless. The viscosity of the overhead fractions increased with increase in overhead temperature, the 90 to 98% fraction being almost semisolid in nature.

The properties of the 11 fractions of hydrogenated polymer I are shown in Table V. In general, such properties as refractive index, density, and per cent carbon show a steady increase with increase in the overhead temperatures of the fractions. A plot of these properties against the volume per cent distilled gives reasonably continuous graphs. The same is true for the molecular weight, with the exception of the 0 to 10% and 30 to 40% fractions. Experimental difficulties in the molecular weight determination were experienced with these particular samples. For this reason the found molecular weights of these two fractions are considered to be in error. To correct these, the experimental values of molecular weight were plotted against the volume per cent distilled, and a reasonable graph was drawn between these points. The values for the molecular weights of the 0 to 10% and 30 to 40% fractions estimated by this procedure are believed to be more nearly correct than the actual experimental values. Table V shows computations based on both the found and estimated values of molecular weight for these two fractions. The experimental molecular weights of the other fractions were used without correction.

Computation of the structural features of all 11 fractions was carried out as for the whole oil, using the previously published analytical scheme (*26*). The complete results are

Table V. Properties and Structural Composition of Distillation Fractions from Hydrogenated Polymer I

Property	Distillation Fraction, Volume %												
	0–10%		10–20%	20–30%	30–40%		40–50%	50–60%	60–70%	70–80%	80–90%	90–98%	Above 98%
Boiling range, ° C.	166–224.5[a]		224.5–248[a]	248–267[a]	185–208[b]		160–178[c]	178–195[c]	195–212[c]	212–235[c]	235–269[c]	269[c]–284[d]	> 284[d]
Refractive index, n_D^{20}	1.4522		1.4649	1.4706	1.4769		1.4847	1.4891	1.4945	1.5005	1.5052	1.5097	1.5040[e]
Density, 20° C.[f]	0.8331		0.8588	0.8686	0.8845		0.8977	0.9070	0.9187	0.9324	0.9420	0.9402[g]	0.9576[g]
Specific dispersion, 20° C.	98.8		98.6	98.5	100.8		98.4	99.6	99.6	100.8	101.0	102.3	97.8[e]
% C, corrected[h]	86.06		86.42	86.46	86.61		86.66	86.83	87.05	87.24	87.29	87.39	87.54
% H, corrected[i]	13.94		13.58	13.54	13.39		13.34	13.17	12.95	12.76	12.71	12.61	12.46
Molecular weight[j]	240[k]	195[l]	205	214	192[k]	225[l]	242	252	262	307	322	371	374
Molecular formula	$C_{17.20}H_{33.19}$	$C_{13.97}H_{26.97}$	$C_{14.75}H_{27.62}$	$C_{15.40}H_{28.75}$	$C_{13.84}H_{25.50}$	$C_{16.22}H_{29.89}$			$C_{19.13}H_{33.92}$	$C_{22.30}H_{38.86}$	$C_{23.40}H_{40.60}$	$C_{26.99}H_{46.41}$	$C_{27.26}H_{46.23}$
Type formula	$C_nH_{2n-1.21}$	$C_nH_{2n-0.97}$	$C_nH_{2n-1.88}$	$C_nH_{2n-2.05}$	$C_nH_{2n-2.18}$	$C_nH_{2n-2.55}$	$C_nH_{2n-2.89}$	$C_nH_{2n-3.52}$	$C_nH_{2n-4.34}$	$C_nH_{2n-5.74}$	$C_nH_{2n-6.20}$	$C_nH_{2n-7.57}$	$C_nH_{2n-8.29}$
Av. No. rings per mole	1.61	1.49	1.94	2.03	2.09	2.28	2.45	2.76	3.17	3.87	4.10	4.79	5.15
Av. ring size, C atoms	4.5	5.2	5.3	5.5	6.0	5.6	5.9	5.7	5.5	5.3	5.4	5.0	5.1
Av. No. C atoms per ring[m]	4.1	4.8	4.7	4.8	5.3	4.9	5.1	4.9	4.7	4.4	4.5	4.1	4.2
Av. No. C atoms per mole	17.2	14.0	14.8	15.4	13.8	16.2	17.5	18.2	19.1	22.3	23.4	27.0	27.3
Av. No. ring C atoms per mole	6.6	7.2	9.1	9.7	11.1	11.2	12.5	13.5	14.9	17.0	18.4	19.6	21.6
Av. No. alkyl C atoms per mole	10.6	6.8	5.7	5.7	2.7	5.0	5.0	4.7	4.2	5.3	5.0	7.4	5.7
% naphthenic C atoms	38.4	51.4	61.4	62.9	80.5	69.2	71.5	74.2	78.0	76.3	78.6	72.6	79.1
% alkyl C atoms	61.6	48.6	38.6	37.1	19.5	30.8	28.5	25.8	22.0	23.7	21.4	27.4	20.9

[a] At 764 mm.
[b] At 100 mm.
[c] At 10 mm.
[d] At 6 mm.
[e] By extrapolation of properties of heptane solutions of solid.
[f] By capillary pycnometer, except for 90–98% fraction and residue.
[g] By ASTM D 70–52.
[h] Corrected % C = 100(%C)/% C + % H.
[i] Corrected % H = 100(%H)/% C + % H.
[j] Ebullioscopic, in benzene (Menzies-Wright).
[k] Found molecular weights.
[l] Molecular weights assumed to be correct, see text.
[m] Assuming 50% condensation.

shown in the lower section of Table V. It was found that the overhead fractions become increasingly more cyclic as the boiling range increases. The number of rings per mole varies from 1.61 in the first 10% to over five rings per mole in the 2% bottoms. A plot of the number of rings per mole against the volume per cent distilled is shown in Figure 4. This indicates that the lowest-boiling components of polymer I probably contain monocyclic molecules. However, the bulk of the material is made up of molecules containing two to four rings per mole.

The average ring size does not show the same trend as the average number of rings per mole. The ring size increases as the distillation proceeds and is at a maximum near the mid-point of the oil, after which it decreases, as shown in Figure 4. Thus, the monocyclic and highly polycyclic portions of the oil seem to contain predominantly five-membered rings, while in the middle portions of the oil six-membered rings are in greater abundance.

The number of naphthenic carbon atoms per mole increases steadily from 7 to 22 from the lowest to the highest boiling fraction (Figure 5). On the other hand, the number of alkyl carbon atoms decreases slowly from seven in the first 10% of the polymer to about four at the 70% point. After this, a slight increase results. Thus, the total difference in alkyl carbon atoms is only about three over the entire oil, in contrast to about a 15-carbon atom spread in naphthenic carbon atoms.

True and Apparent Olefinicity. To determine the true number of olefinic double bonds it is necessary to know the percentages of hydrogen in the original and hydrogenated oils. To carry out such an analysis on the distillation fractions of an unknown oil would, theoretically, require a separate hydrogenation of each fraction. This can be an exceedingly time-consuming procedure, particularly if as many as 10 distillation fractions are examined.

As a practical compromise it has been found convenient in this laboratory to examine analogous fractions from the distillation of both the original and hydrogenated polymers. This requires only one hydrogenation. Both the original and hydrogenated oils are distilled, and the corresponding volume per cent fractions are compared. In using such a procedure, it is assumed, for example, that the 5 to 10% by volume fraction of hydrogenated polymer will be more or less identical with the material obtained by hydrogenating the 5 to 10% fraction of original polymer. This assumption will be strictly true only if the boiling points of all the hydrogenated compounds are in the same relationship to each other as the boiling points of the corresponding unhydrogenated compounds, and any azeotroping effects are in the same direction for original and hydrogenated mixtures. While these conditions are reasonably true in general, there are exceptions. However, in view of the tremendous number of compounds present in these oils, it is believed that exceptions may cancel out or be negligible in extent. Any errors introduced by incorrectness of these

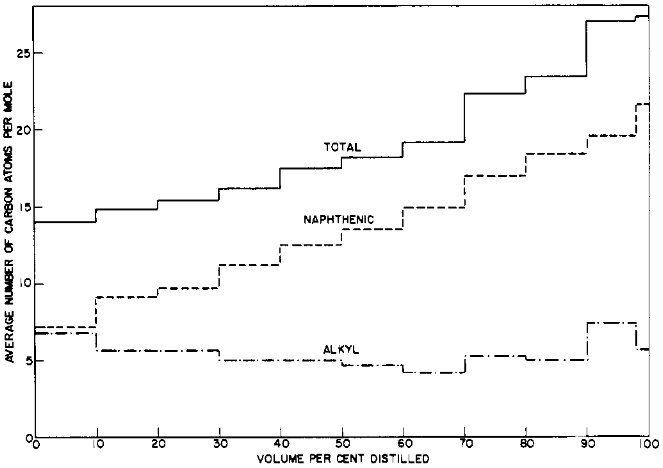

Figure 5. Carbon atom distribution in distillation fractions from hydrogenated polymer I

Table VI. True and Apparent Olefinicity of Selected Fractions from Conjunct Polymer I

	Distillation Fraction (by Volume)			
Property	5–10%	40–45%	70–75%	Bottoms above 90%
Original oil fraction				
Molecular weight[a]	178	228	239	285
Iodine No.	565	488	477	410[a]
MAV	555	344	286	190[a]
Hydrogen, wt. %	11.80	11.52	11.42	10.22
Hydrogenated oil fraction				
Molecular weight[a]	187	233	285	372
Hydrogen, wt. %[a]	13.96	13.37	12.85	12.58
Computations				
Apparent No. of double bonds per mole (by iodine No.)	4.0	4.4	4.5	4.6
True No. of double bonds per mole (by hydrogenation)				
From original molecular weight	2.2	2.4	2.0	3.8
From hydrogenated molecular weight	2.3	2.4	2.3	4.8
Average	2.3	2.4	2.2	4.3
% error by iodine No.	74	83	105	7
No. of conjugated double bonds per mole	2.0	1.6	1.4	1.1
No. of isolated double bonds per mole	0.3	0.8	0.8	3.2
% conjugation	87	67	64	26

[a] Estimated from graph of corresponding properties *vs.* volume per cent distilled.

assumptions are believed to be within the over-all experimental error of the analytical scheme.

Table VI compares the properties of four 5% fractions of original polymer I with the properties of the corresponding fractions of hydrogenated polymer I. From these data, the olefinicity and conjugation of the original fractions are computed. Because of some uncertainty in the molecular weights of the two highest boiling fractions, the true number of double bonds for each fraction was computed from two separate equations, using the molecular weights of both the original and hydrogenated samples. Lipkin, Sankin, and Martin (*23*) have presented equations for making both these calculations. The results of these two methods compared well for all the fractions except the bottoms above 90%. For this case, the average of both methods was selected as being least subject to error.

The main portion of conjunct polymer I is essentially diolefinic, as shown by the data in Table VI. The whole oil appears approximately triolefinic (Table IV) because of the predominance of tetraolefins at the heavier ends. In the lower-boiling portions of the oil, the double bond pair is largely conjugated. Near the middle part of the oil and the 75% point, about ⅔ of the double bonds are in conjugation; at the high-boiling ends the conjugation has decreased to about 25%, which means one conjugated pair in each eight double bonds. The analytical results on the fractions agree reasonably well with the over-all conjugation of 64% on the undistilled oil. A possible explanation for the decreased conjugation of the higher fractions is given in the discussion.

The errors which may result if the olefinicity is based on the iodine numbers of the fractions are again emphasized by the data shown in Table VI. Type formulas (not shown in the table) confirm the correctness of the olefinicity determined by hydrogenation.

Possible Structures in Conjunct Polymer I. One objective of structural data is to permit the drawing of logical structural formulas for molecular types present in the conjunct polymers. This has been done for conjunct polymer I, using the data of Tables V and VI, supplemented by the ultraviolet and infrared spectra. These data are based on average compositions. Therefore, a leeway of several carbon atoms, plus or minus, is allowed in the formulas.

Figures 6 to 10 illustrate examples of molecular types which may be present in conjunct polymer I. These are classified according to molecular size. The 0 to 10% fraction of the polymer has an average of 1.49 rings per mole (Table V). By graphical interpolation, it is estimated that the hydrocarbons in the first few per cent of the oil are monocyclic, and that the average molecule contains approximately 10 carbon atoms per mole. The rings are essentially five-membered, and five to six carbon atoms are present in short side chains. Structural formulas for compounds in the first few per cent of distillate also need to show approximately two double bonds in heteroannular conjugation and a preponderance of tertiary and quaternary substitution. Methylene and vinyl groups must be absent. Moreover, the arrangement of double bonds and substituents should be such as to give a calculated ultraviolet absorption maximum (by Woodward's rules) of 242 mμ, which is the value observed for the 0 to 5% fraction. Figure 6 illustrates three types of compounds which conform to all these requirements and may be considered as possible constituents of polymer I. In each case an exocyclic double bond must be present.

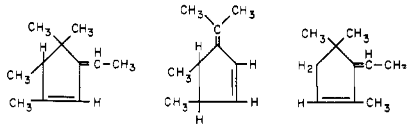

Figure 6. Probable structures of typical monocyclic molecules in polymer I

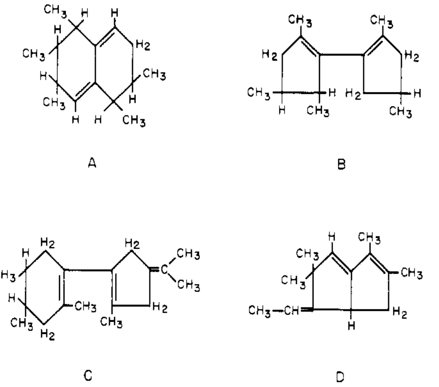

Figure 7. Probable structures of typical dicyclic molecules in polymer I

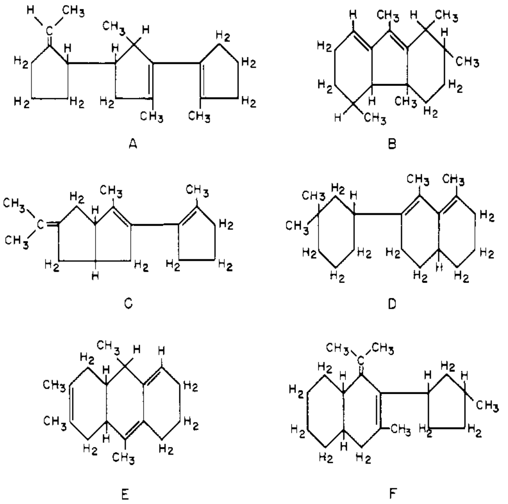

Figure 8. Probable structures of typical tricyclic molecules in polymer I

Between the first few per cent of distillate and the 20% point the compounds present in polymer I appear to be mixtures of mono- and dicyclic molecules. At the 20 to 30 volume % point the fractions are, on the average, almost purely dicyclic and have a ring size indicating both cyclopentane and cyclohexane types. There are about 2.3 double bonds per mole, about 1.5 of which are conjugated. About 9 to 10 carbon atoms are in rings and 5 to 6 in side chains, and the absorption maximum is approximately 247 mμ. A mixture of compounds such as shown in Figure 7, A and B, satisfies most of these requirements. These are deliberately shown both as condensed and uncondensed molecules, inasmuch as the extent of condensation of the rings is not known. Compounds A and B show heteroannular conjugation and their absorption maxima compute to 247 mμ by Woodward's rules. In compound B this is achieved entirely by substitution on the conjugated pair. In compound A, whose conjugated pair is not completely substituted, the additional required 10 mμ are obtained from two exocyclic double bonds. Since the 20 to 30% fraction also contains isolated double bonds, it is assumed that a smaller proportion of triolefins, such as compounds C and D, might be present. These both have calculated absorption maxima of 247 mμ. In the case of compound C

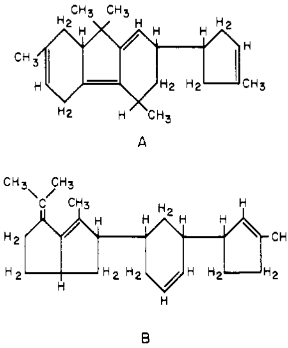

Figure 9. Probable structures of typical tetracyclic molecules in polymer I

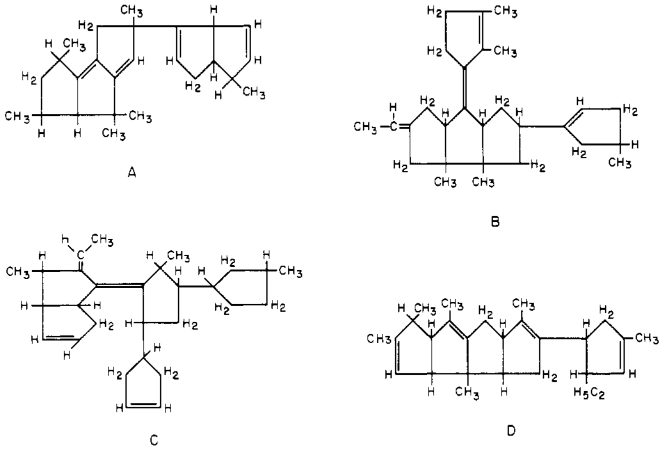

Figure 10. Probable structures of typical pentacyclic molecules in polymer I

this is achieved by six alkyl (or ring residue) substituents on the conjugated pair, while for D it is accomplished by five substituents and one exocyclic double bond involved in the conjugated pair. In both cases the exocyclic double bond which is not a part of the conjugated system is assumed not to affect the absorption maximum.

Between the 20 to 30% fraction and the 60 to 70% fraction the composition of polymer I is adequately represented by mixtures of di- and tricyclic molecules made up of cyclopentane and cyclohexane rings with varying numbers of double bonds, partly in conjugation.

The 60 to 70% fraction of polymer I is essentially tricyclic, with approximately 14 to 15 ring carbon atoms and 4 to 5 alkyl carbon atoms. Both di- and triolefins are present, about ⅔ of the double bonds being conjugated. Some possible types of molecules which may be present in this fraction are shown in Figure 8. Both condensed and uncondensed molecules containing five- and six-membered rings are shown. Two of these molecules (A and C) have calculated absorption maxima of 247 mμ and four (B, D, E, and F) have calculated maxima of 252 mμ.

The fractions above the 60 to 70% point become increasingly difficult to depict, because of the tremendous number of possible structures which may be drawn that satisfy the known data. Figure 9 illustrates some tetracyclic and Figure 10 some pentacyclic molecules which are possible types in the highest boiling ends of polymer I. The tetracyclics are shown as mixtures of five- and six-membered rings, but the pentacyclics are shown as five-membered rings only (compare Figure 4). All the structures are drawn to conform approximately with the requirements in Table V regarding the distribution of alkyl and ring carbon atoms. Mixtures of condensed and uncondensed rings are assumed. The two tetracyclics which are illustrated (A and B) have calculated absorption maxima of 257 mμ. In A this is achieved by the fact that one double bond of the conjugated pair is exocyclic to one ring, while the other double bond is exocyclic to two rings. All of the pentacyclic molecules except D which are illustrated have calculated absorption maxima of 257 mμ. Since the molecules in the high-boiling ends are less conjugated than in the lower-boiling fractions, a greater proportion of isolated double bonds is indicated, compound D being entirely unconjugated.

DISCUSSION

Ring Substitution. The number of alkyl and/or alkenyl substituents on the ring carbon atoms of the hydrocarbons present in conjunct polymers varies appreciably for different samples. The structural formulas shown in Figures 6 to 10 indicate that polymer I has a considerable number of unsubstituted ring positions. On the other hand, Table III reveals that polymer I also has the lowest ratio of alkyl carbon atoms to ring carbon atoms of the five examples cited. This may mean that polymer I is not a typical example with respect to the degree of ring substitution. In fact, Bloch (*2*, *4*) proposed formulas for the monocyclic fractions of conjunct polymers in which nearly all possible ring positions are substituted. The extent of ring substitution in these materials is probably influenced by many factors, such as the conditions under which they are produced and recovered.

Ring Size. A logical mechanism for the formation of conjunct polymers has been proposed by Bloch (*2*). This mechanism is based on the cyclization of an intermediate carbonium ion, and favors the formation of five-membered rings. Consequently, Bloch's proposed structures for the types of molecules present in conjunct polymers are limited to five-membered rings. Moreover, he reported that when hydrogenated conjunct polymers were treated with dehydrogenation catalysts, substantially no simple dehydrogenation to aromatic hydrocarbons occurred (*4*). This fact casts doubt on the existence of six-membered rings in the polymers examined in his laboratory.

The monocyclic fraction from conjunct polymer I has, within experimental error, an average ring size of five (cf. Table V). In this respect the formulas for compounds present in this fraction agree with Bloch's formulas. On the other hand, the data of Tables III and V indicate that higher fractions from polymer I, as well as other conjunct polymers studied in this laboratory, are not restricted to five-membered rings. These data, which are based on the well-known Kurtz-Lipkin correlations, point to average ring sizes both greater and smaller than 5.0. It is possible that the average ring size, like the extent of ring substitution, may be dependent on a number of factors. Admittedly, it would be highly desirable to obtain more data from other laboratories on the question of ring sizes in conjunct polymers.

It is important to understand that the ring size found by correlation methods is an average number. Thus, an equimolar mixture of five-membered and six-membered rings has a theoretical ring size of 5.5. Consequently, a ring size in the neighborhood of 6.0 does not restrict the sample to cyclohexane rings. This fact lends great interest to a report of Bloch's that certain conjunct polymers obtained in his laboratory yielded small fractions having a pronounced blue color, suggesting the presence of azulenes (*4*). Inasmuch as the azulene system consists of a seven-membered ring fused to a five-membered ring, its average ring size is 6.0. Bloch's observation thus lends weight to the possibility that conjunct polymers may contain compounds of more than one ring size. In fact, Oblad has suggested the possibility that an equilibrium may exist between rings of different sizes in the original conjunct polymer–catalyst complex (*28*).

The structural formulas shown in this paper are limited to five- and six-membered rings. The evidence presented, however, suggests that these unusual materials may be even more complex than the formulas of Figures 6 to 10 indicate. This is a fruitful field for additional research, and it is hoped that other laboratories will investigate this problem.

Mass Spectrometry. More recently Meyerson (*25*) provided a different approach to the structure of conjunct polymers by the application of low-voltage mass spectrometry. He examined a conjunct polymer from the treatment of a branched-chain alkane with aluminum chloride, and found unsaturated species containing from 10 to 37 carbon atoms. Type formulas C_nH_{2n-2} to C_nH_{2n-14}, and possibly beyond, were noted. Below a carbon number of C_{16} the most abundant type was C_nH_{2n-4}. This corresponds to the type formulas of monocyclic structures shown in Figure 6. From C_{16} to C_{23}, the most abundant type was C_nH_{2n-8} (corresponding to the structures of Figure 7) and above C_{23}, C_nH_{2n-12}.

Meyerson observed that according to these formulas the conjunct polymer consisted largely of isomeric cyclodienes (C_nH_{2n-4}) and their dimers (C_nH_{2n-8}) and trimers (C_nH_{2n-12}). He pointed out that this could explain why the extent of conjugation of conjunct polymer I decreased markedly from the lower boiling to the higher boiling fractions (Table VI). Polymerization would be expected to involve conjugated double bonds preferentially, leaving an isolated double bond in place of a conjugated pair.

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