chloride. The methylcreatinine hydrochloride thus obtained melted with slight decomposition at 234–236°, as reported. All attempts to condense this product with benzaldehyde, either by the usual procedure or with longer heating and increased proportions of sodium acetate and of acetic anhydride, were completely unsuccessful.

At this stage it was thought worth while to show that the methylation could not have taken place with the introduction of a second methyl group on the 1-nitrogen. The methylcreatinine was accordingly hydrolyzed and found to yield sarcosine and methylamine. Since it was thus clear that the substance must have one of the two structures represented by VIII and IX, it was sought to convert it into a mixture of these two isomers (see discussion) in the hope that at least one of them might be condensed with benzaldehyde. The mixture obtained, however, gave no benzal derivative.

Summary

1. Benzalcreatinine and a number of new compounds derived from it have been described.

2. N-Methylphenylalanine may conveniently be prepared by the reduction and subsequent hydrolysis of benzalcreatinine.

3. Methylation of benzalcreatinine takes place first on the nitrogen atom in position 2. N-Methylcreatinine does not condense with benzaldehyde.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MCGILL UNIVERSITY]

THE POLYMERIZATION OF INDENE, CINNAMAL FLUORENE AND SOME DERIVATIVES OF INDENE

BY GEORGE STAFFORD WHITBY AND MORRIS KATZ

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Indene is known to be polymerizable by concentrated sulfuric acid, heat and other means.[1] The polymerizing agencies used in the present work were heat, antimony pentachloride and stannic chloride. The two latter were found to yield polymers higher than any previously obtained.[2] The molecular weight of the $SbCl_5$ product corresponded approximately to that of a molecule derived by the union of 15 indene molecules, while that of the $SnCl_4$ product corresponded approximately to the union of 25 indene molecules. Although these polymers are thus comparatively high, they do not show the properties of lyophilic colloids. Further, they do not represent chemical individuals but, rather, as was shown by fractionation, mixtures representing widely different degrees of polymeri-

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[1] (a) Krämer and Spilker, *Ber.*, **23**, 3276 (1890); (b) **33**, 2260 (1900); (c) Weger, *Z. angew. Chem.*, **22**, 345 (1909); (d) Weger and Billmann, *Ber.*, **36**, 640 (1903); (e) Weissgerber, *Ber.*, **44**, 1438 (1911); (f) Guntz and Minguin, *Compt. rend.*, **152**, 373 (1911); (g) Ciamician and Silber, *Ber.*, **46**, 420 (1913); (h) Stobbe and Färber, *Ber.*, **57**, 1838 (1924); (i) Staudinger, *Ber.*, **59**, 3019 (1926); (j) Bruson, *Diss.*, Zürich (1925); (k) *Ber.*, **60**, 1094 (1927).

[2] Since the present work was complete some data on the polymeric product obtained from indene by $SnCl_4$ have been published by Staudinger, ref. 1 i.

zation.[3] From the $SnCl_4$ product there was obtained at one extreme a fraction $(C_9H_8)_8$ and at the other a fraction $(C_9H_8)_{29}$.

The polymerization of indene by heat was followed at various temperatures and was found to take place the more rapidly the higher the temperature. At a given temperature, the molecular weight of the product was found to rise as the proportion of the indene which had undergone polymerization increased. The molecular magnitude ultimately attained when polymerization had become substantially complete appeared to be lower, the higher the temperature employed. Thus, at 200°, when polymerization was 96.75% complete, the molecular weight was 676, whereas at 178°, when polymerization was only 82.24% complete, it was 886.[4] The explanation of the fact that the higher the temperature at which polymerization is brought about, the lower is the molecular weight of the product ultimately obtained, is not improbably similar to that which Staudinger[1l] has suggested in the case of styrene, namely, that "cracking" sets a limit to the size of polymeric molecule which can exist at a given temperature.

Like the $SbCl_5$ and $SnCl_4$ polymers, the heat polymers are heterogeneous.

There is a clear relationship between the melting points and molecular weights of the polyindenes, the former rising regularly with increase in the latter. Fig. 1 shows the data in this connection for all the 39 samples of polyindene described in the experimental part. The relation between melting point and molecular weight can hardly be expected to be very close in view of the errors attendant on the determination of the high molecular weights and of the fact that the products are amorphous mixtures. There has also been included in the figure points representing products described by previous workers, namely, a dimer,[1h] three thermopolymers,[1h,k,j] two photo-polymers,[1h] and a sulfuric acid polymer.[1j] These all agree reasonably well, considering the circumstances, with the relationship found for the products of the present investigation. It would appear that the polymers of indene, no matter by which of the known means they are produced, form a regular and unbroken series, increasing in melting point with increase in the degree of polymerization.

Fifteen samples of polyindene (7 by $SnCl_4$, 8 by heat), the bromine absorption of which was measured, all showed substantially the same degree of unsaturation per molar weight, namely, that represented by the absorption of two atoms of bromine. Hence all the polyindene molecules, no matter what their size, contain one double bond.

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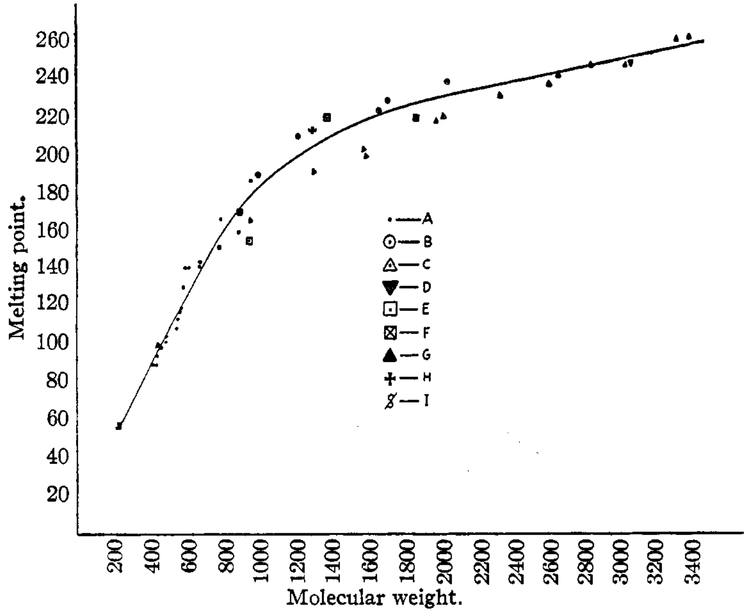
[3] Products of the polymerization of indene to which authors have assigned names carrying the suggestion that the products are chemical individuals (see refs. 1 c and 1 k) are, in the light of the present investigation, almost certainly mixtures.

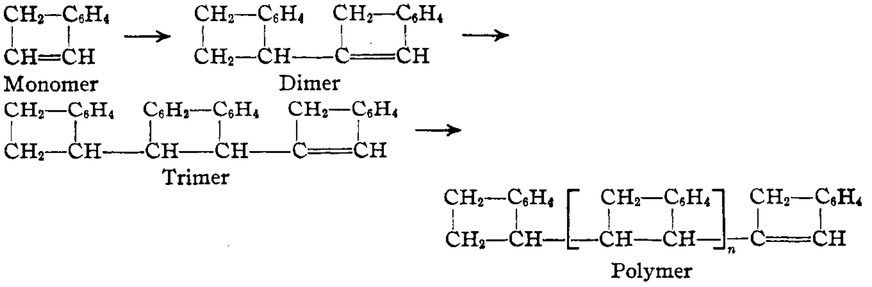
[4] At 260° a product with a molecular weight of 467 was obtained by Bruson (ref. 1 k) by heating for 25 hours—a period sufficient, to judge by the present investigation, for complete polymerization.

In the light of these facts the polymerization of indene is best represented as proceeding step-wise by the addition regularly of successive molecules of monomer to the double bond present at the stage of polymerization immediately preceding, according to a scheme such as the following



A, Thermo-polymers; B, by $SbCl_5$; C, by $SnCl_4$; D, by $SnCl_4$, Bruson, ref. 1i; E, thermo-polymers, Stobbe and Färber, ref. 1h; F, photo-polymers, Stobbe and Färber, ref. 1h; G, thermo-polymers, Bruson, ref. 1k; H, by H_2SO_4, Bruson, ref. 1i; I, di-indene, Stobbe and Färber, ref. 1h.

Fig. 1.—Polymers of indene.



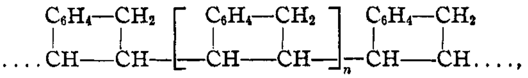
$$\underset{\text{Monomer}}{\begin{array}{l}\mathrm{CH_2{-}C_6H_4}\\ \ \,|\qquad\ |\\ \mathrm{CH{=}CH}\end{array}} \longrightarrow \underset{\text{Dimer}}{\begin{array}{l}\mathrm{CH_2{-}C_6H_4\quad CH_2{-}C_6H_4}\\ \ \,|\qquad\ |\qquad\qquad |\qquad\ |\\ \mathrm{CH_2{-}CH{-\!-}C{=\!=}CH}\end{array}} \longrightarrow$$

$$\underset{\text{Trimer}}{\begin{array}{l}\mathrm{CH_2{-}C_6H_4\quad C_6H_2{-}C_6H_4\quad CH_2{-}C_6H_4}\\ \ \,|\qquad\ |\qquad\quad |\qquad\ |\qquad\quad |\qquad\ |\\ \mathrm{CH_2{-}CH{-\!-}CH{-\!-}CH{-\!-}C{=\!=}CH}\end{array}} \longrightarrow$$

$$\underset{\text{Polymer}}{\begin{array}{l}\mathrm{CH_2{-}C_6H_4}\left[\begin{array}{l}\mathrm{CH_2{-}C_6H_4}\\ \ \,|\qquad\ |\\ \mathrm{{-}CH{-}CH{-}}\end{array}\right]_n\mathrm{CH_2{-}C_6H_4}\\ \ \,|\qquad\ |\qquad\qquad\qquad\qquad\qquad |\qquad\ |\\ \mathrm{CH_2{-}CH{-}\qquad\qquad\qquad\quad{-}C{=\!=}CH}\end{array}}$$

There are in all four possible similar schemes involving the wandering of a hydrogen atom from the addendum, but the above is chosen because it accords best with both the facts (a) that the polyindenes decompose largely to indene on dry distillation and (b) that the dimer of indene which has been previously described in the literature,[1h] and which, because of its melting point (see Fig. 1) and its polymerizability,[1h] probably lies on the direct path from indene to the polyindenes, gives α-hydrindone on oxidation.

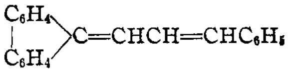
The mode of formulation of polyindenes suggested by Staudinger,[1i] namely,



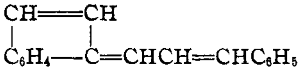
$$\begin{array}{cccccccccccc} & C_6H_4 & - & CH_2 & \Big[& C_6H_4 & - & CH_2 & \Big] & C_6H_4 & - & CH_2 \\ & | & & | & & | & & | & & | & & | \\ \ldots & CH & - & CH & - & CH & - & CH & -_n & CH & - & CH\ldots, \end{array}$$

which represents the polymerization as due to the coming together of a number of monomeric molecules without the wandering of hydrogen atoms, is out of accord with the fact that the polyindenes are unsaturated, see above, since the free terminal valencies shown in such a method of formulating polymeric products are, on account of the size of the molecule, not regarded as conferring unsaturation.[5] Further, in the case of the lower polymers of indene which are obtained by means of heat and which may contain as few as four indene molecules, such a structure could hardly be stable: it would almost certainly undergo rearrangement to a structure containing an ethylene linkage.

A considerable number of cinnamal compounds have been shown to be photo-polymerizable to dimers.[6] In the present investigation it has been found that the hydrocarbons cinnamal fluorene (I) and cinnamal indene (II) are capable of yielding higher, albeit non-colloidal, polymers.



I



$$\begin{array}{lll} CH & = & CH \\ | & & | \\ C_6H_4 & - & C=CHCH=CHC_6H_5 \end{array}$$

II

Cinnamal fluorene has been stated by Ostromislenski[7] to yield when heated in boiling acetic acid a polymeric product which shows elastic properties; which, when stretched and then released, slowly retracts partially during one or two days. The present authors were unable to secure polymerization of cinnamal fluorene by treatment with acetic acid at any temperature, and the polymers obtained by other means were entirely lacking in elasticity. Heating it alone at 200° for two to three weeks was found to convert cinnamal fluorene into a low polymer, and at 240–250° for three days into a higher polymer corresponding approximately in mean molecular weight to a nonamer. Antimony pentachloride produced a polymer corresponding approximately to an octamer. Fractionation showed the material to be a mixture. Similarly, cinnamal

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[5] Staudinger, *Ber.*, **53**, 1073 (1920); Staudinger and Fritschi, *Helv. Chim. Acta*, **5**, 787 (1922).

[6] See, for example, (a) Riiber, *Ber.*, **35**, 2414 (1902); (b) **46**, 338 (1913); (c) Ruhemann, *J. Chem. Soc.*, **85**, 1453 (1904); (d) Reimer, *Am. Chem. J.*, **45**, 417 (1911); (e) Stobbe, *Ber.*, **45**, 3396 (1912); (f) *J. prakt. Chem.*, **110**, 129 (1925).

[7] Ostromislenski, *J. Russ. Phys.-Chem. Soc.*, **47**, 1374 (1915).

indene was polymerized by heat, by $SbCl_5$ and by $SnCl_4$, and the products were shown to be heterogeneous. Figs. 2 and 3 show that there is a linear relation between the melting point and the molecular weight of the polymers both in the case of cinnamal fluorene and cinnamal indene.

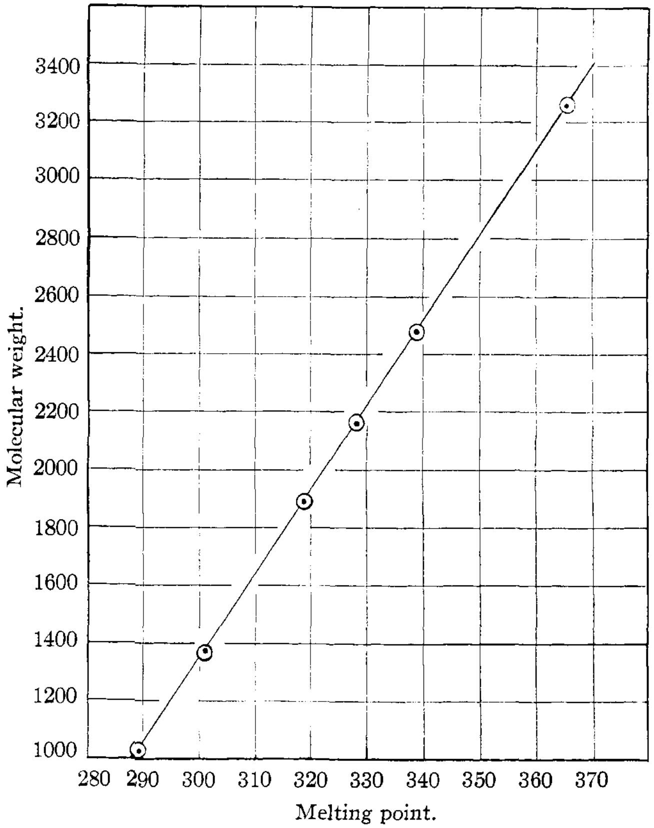
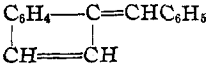


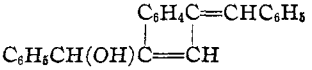
Fig. 2.—Polymers of cinnamal fluorene (by $SbCl_5$).

Other compounds investigated were benzal indene (III) and hydroxybenzyl indene (IV).



$$\begin{array}{ll} C_6H_4\text{—}C{=}CHC_6H_5 \\ | \qquad\quad | \\ CH{=\!=}CH \end{array}$$

(III)



$$\begin{array}{r} C_6H_4C{=}CHC_6H_5 \\ | \quad | \qquad\qquad \\ C_6H_5CH(OH)C{=\!=}CH \end{array}$$

(IV)

Each of the substances with the polymerization of which the present communication deals contains a conjugated system although, except in the case of the cinnamal compounds, it is not of the typical, open-chain kind. In indene the conjugated system, the presence of which is clearly shown by the magnetic rotatory power,[8] is of what may be called

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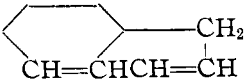
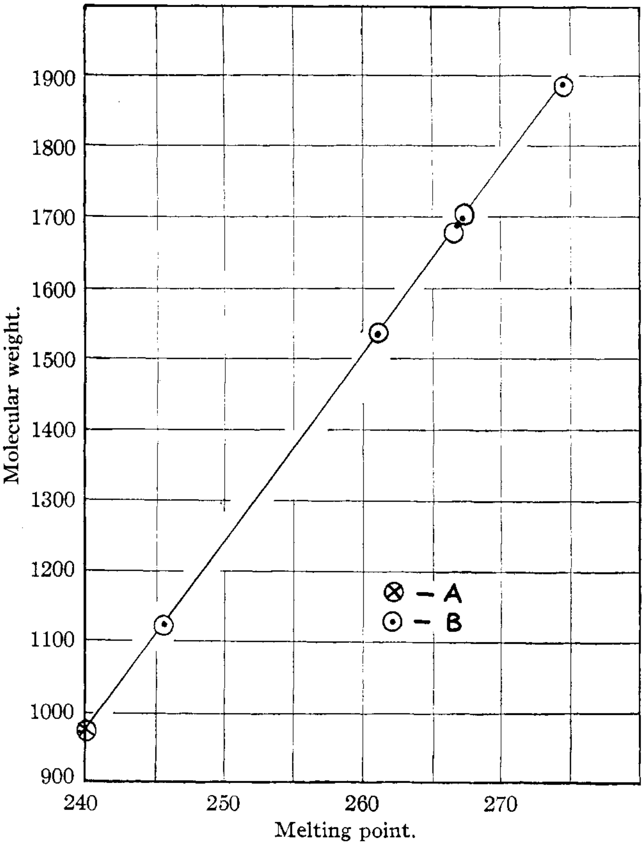
[8] Smiles, "The Relation between Chemical Constitution and Some Physical Properties," Longmans Green and Co., London, **1910**, p. 489.

the semi-benzenoid type shown in the following formulation:



In this connection it may be mentioned that preliminary experiments have shown that isoeugenol and isosafrole, both of which, as is proved by physical measurements,[8] contain semi-benzenoid conjugated systems, are polymerizable by $SbCl_5$ and by heating at 200° far more readily than the isomeric compounds, eugenol and safrole, respectively, in which such a system is lacking.[9]



A, $SnCl_4$ polymer; B, thermo-polymers.

Fig. 3.—Polymers of cinnamal indene.

Experimental Part

Indene

The indene used was a pure, colorless sample obtained by several distillations with a fractionating column and boiling at 181–181.5°.

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[9] It is desired to reserve the further investigation of this matter (G. S. W.).

Polymerization by (a) Antimony Pentachloride, (b) Stannic Chloride.—To 10 cc. of indene diluted with an equal volume of chloroform was added 1 cc. of a 20% solution of the chloride in chloroform. The solution became red and warm, a good deal of the chloroform boiling off. After ten minutes it was diluted with 10 cc. more chloroform, and then poured into 100 cc. of absolute alcohol. The precipitated polymeric product was separated, dissolved in benzene and reprecipitated by alcohol, this process being repeated three times. The polyindene thus obtained in quantitative yield as a white powder was free from all traces of the catalyst. A larger batch was prepared in a similar way, starting with 70 cc. of indene and treating with $SnCl_4$. The products were separated into fractions by precipitation with alcohol from benzene solution. In the case of the larger batch of polymer by $SnCl_4$, the last fraction was isolated by removing a considerable proportion of the solvent, adding water, separating the benzene layer and allowing it to evaporate at room temperature. In the case of these and all other polymeric products described herein melting points were taken by the electrically heated apparatus of Mason;[10] molecular weights were determined cryoscopically in benzene unless otherwise stated and the viscosity of 1% solutions in benzene was measured in an Ostwald viscosimeter at 25°. The bromine absorption of seven fractions of the larger batch of polyindene prepared by the aid of $SnCl_4$ was measured by allowing a solution of 1.5–3 g. in 25 cc. of chloroform to stand in the dark for twenty-four hours at room temperature with 25–50 cc. of 0.07 *N* bromine in chloroform. Preliminary experiments

Table I

Polyindene by Stannic Chloride

First batch

Fraction	M. p., °C.	Mol. wt.	Viscosity (time of flow in secs.)[a]
Before fractionation	247–250	2971	
1	261–264	3254	84.2
2	242–244	2608	81.2
3	217–220	1950	79.0
4	202–204	1558	77.0
5	190–193	1287	74.8

Second batch

Fraction	M. p., °C.	Mol. wt.	Bromine absorption, (atoms per mol.)
1	261–265	3320	2.43
2	247–250	2785	2.06
3	236–241	2560	2.12
4	231–235	2295	1.97
5	219–223	1990	1.85
6	198–201	1568	2.19
7	164–167	952	1.93

Polyindene by $SbCl_5$

Fraction	M. p., °C.	Mol. wt.	Viscosity (time of flow in secs.)
Before fractionation	228–230	1687	
1	238–240	2013	78.6
2	223–225	1642	76.8
3	209–211	1204	74.2
4	188–191	990	73.0

[a] Time of flow of benzene, 67 secs.; of 1% indene in benzene, 68.6 secs.

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[10] Mason, *J. Soc. Chem. Ind.*, **45**, 199 (1926).

had shown that the absorption of bromine was only about 85% complete after four and one-half hours at room temperature but was complete after twenty-four hours. They also showed that indene gave the theoretical amount of absorption by the procedure followed. Data are given in Table I. When dry distilled under a pressure of 2 mm., the $SnCl_4$ polymeric product gave a considerable quantity of indene and also some higher boiling material, which probably consists of low polymers, and which will be further examined.

Polymerization by Heat.—Samples of indene, each about 5 g. in weight, were heated in sealed tubes for various periods at 200, 178, 140 and 100°. The percentage of polymerization was determined by distilling off unchanged indene at 75° under reduced pressure, extracting the residue with ether in a Soxhlet in order to eliminate any (insoluble) truxene (no truxene was in fact found in any of the samples), pouring the ether extract into twice its volume of alcohol, collecting the white polyindene and drying it *in vacuo*. The bromine absorption of some of the products was determined by allowing a solution of about 0.8 g. in 25 cc. of chloroform to stand in the dark for twenty-two hours at room temperature with 60 cc. of 0.1 *N* bromine in chloroform. (Indene in the form of Wijs solution was not absorbed by any of the products.) The following data were obtained.

TABLE II

THERMO-POLYMERIZATION OF INDENE

Period of heating, days	Polymerization, %	M. p. of polymer, °C.	Mol. wt. of polymer	Bromine absorption, atoms per mol.
		At 200°		
1	22.7	103–105	490	
2	38.7	107–109	545	
3	49.1	112–114	553	2.00
4	76.35	128–132	586	1.96
8	89.3	139–142	615	
21	96.75	142–145	676[a]	
		At 178°		
1	5.02	88–90	419	
2	12.4	93–95	442	
3	18.55	97–100	462	
4	26.3	103–105	493	
11	65.5	116–118	566	1.99
16	70.6	140–142	669	2.11
19	74.15	150–152	778	2.11
30	82.2	158–160	886[b]	
		At 140°		
25	15.9	89–90	414	2.03
70	45.35	118–120	574	2.07
		At 100°		
70	2.65			

[a] C, 92.90; H, 7.08.

[b] C, 92.95; H, 7.04 (calcd. for $(C_9H_8)_x$: 93.10, 6.90).

The polymeric product obtained from 10 g. of indene by eight days' heating at 200° was dissolved in 200 cc. of ether and fractionally precipitated by the addition of absolute alcohol in approximately the following amounts: 20, 20, 40, 50 and 75 cc., the precipitate being filtered off after each addition. The following table shows the results obtained.

TABLE III

FRACTIONATION OF THERMO-POLYMERIZED INDENE

Fraction	Before fractionation	1[a]	2	3	4	5
M. p.....	139–142°	185–188°	165–167°	139–142°	100–102°	88–90°
Mol. wt..	615	948	787	594	491	438

[a] Bromine absorption, 1.94 atoms per mol.

Cinnamal Fluorene

Cinnamal fluorene was prepared according to the directions of Thiele and Henle.[11] It was found that by using absolute alcohol prepared with the aid of calcium instead of commercial absolute alcohol a yield of 25 g. from 40 g. of fluorene was obtained instead of 18–21 g. as mentioned by Thiele and Henle; m. p. 155.5° (from benzene).[12]

Thermo-polymerization.—(a) Solutions of 3 g. of cinnamal fluorene in 50 cc. of liquid were heated at the boiling point in each of the following solvents: toluene (110°), acetic acid (118°), xylene (140°) and tetrahydronaphthalene (207°) for periods ranging in each case from twelve hours to two weeks. In no case was there any evidence of polymerization, the melting point of the material in solution being 155° in every case. (b) Solutions of 5 g. of cinnamal fluorene in 25 cc. of acetic acid were heated in sealed tubes at 125° and at intervals of 10° up to 175° for periods in each case up to one week. In every case only unchanged cinnamal fluorene could be recovered. (c) Samples of cinnamal fluorene heated alone for one week at temperatures up to 190° showed no polymerization. After heating at 200° for three weeks a small amount of polymerization occurred and by solution in benzene followed by precipitation with absolute alcohol, there was obtained a red-brown, amorphous powder; m. p., 168–170°; mol. wt., 570 (calcd. for $(C_{22}H_{16})_2$: 560). (d) Cinnamal fluorene was heated in a sealed tube at 240–250° for three days; the product was dissolved in a large volume of benzene and the reddish powder which came out on cooling was collected and dried *in vacuo;* m. p., 356–370°; mol. wt. (Rast's method in camphor), 2558; C, 93.90; H, 5.74 (calcd. for $(C_{22}H_{16})_9$: 2520, 94.28, 5.72). The product was soluble in cold benzene, in chloroform and in carbon tetrachloride with difficulty; more easily soluble in hot benzene and in acetone; insoluble in alcohol, ether, acetic acid and petrolic ether. Like the other polymeric products obtained from cinnamal fluorene, it gave deep red solutions. (Solutions of unpolymerized cinnamal fluorene are yellow.) When dry distilled it yielded cinnamal fluorene.

Polymerization by Antimony Pentachloride.—To a solution of 10 g. of cinnamal fluorene in 250 cc. of chloroform was added 12 cc. of a 20% solution of $SbCl_5$ in chloroform. The solution turned violet in color, then deep blue and became warm. After

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[11] Thiele and Henle, *Ann.*, **347**, 303–304 (1906).

[12] A red, somewhat sticky by-product formed during the condensation of fluorene and cinnamic aldehyde was examined, after being freed from cinnamal fluorene by means of acetone, in which it was more soluble than cinnamal fluorene. This material could be stretched, and it seems possible that it was a similar product that Ostromislenski (ref. 7) described as an elastic polymer of cinnamal fluorene. Although the material could be stretched, it showed no elasticity, as it entirely failed to retract after being extended. It was soluble in hot alcohol and was not improbably a condensation product of two molecules of cinnamic aldehyde, because (a) the molecular weight was 276, and (b) a similar red, amorphous product could be prepared by treating cinnamic aldehyde with sodium ethylate in the absence of fluorene.

standing for four hours, it was poured into 500 cc. of absolute alcohol, which decomposed the complex addition product and caused separation of the polymer. The latter was collected, dissolved in benzene and reprecipitated with alcohol. This purification was repeated four times and the final product, consisting of a dark yellow powder free from catalyst, was dried *in vacuo;* yield, 8.2 g.; m. p., 327–329°; C, 93.89; H, 5.80; molecular weight, 2240 (calcd. for $(C_{22}H_{16})_8$: 94.28, 5.72, 2240). The polymer was soluble in benzene, xylene, chloroform, carbon tetrachloride; insoluble in alcohol, ether and acetic acid. It was separated into fractions by the addition of successive quantities of alcohol to a solution of 15 g. of the polymer in 800 cc. of benzene, the total weight of the five fractions collected being 14.5 g. The properties of the fractions are shown in the following table.

TABLE IV

PROPERTIES OF THE FRACTIONS

Fraction	M. p., °C.	Molecular weight (Rast's method in camphor)	Approx. no. of monomeric mols. per av. mol. of polymer	Viscosity, time of flow of 1% soln. in benzene[a]
1	365–368	3275	12	90.7 secs.
2	336–338	2485	9	86.4
3	317–319	1897	7	82.3
4	302–305	1380	5	81.0
5	286–290	1034	4	78.0

[a] Time of flow of (a) benzene, 67.0 secs.; (b) 1% solution of unpolymerized cinnamal fluorene, 69.4 secs.

Antimony pentachloride was selected as the most active agent for the purpose of bringing about the catalytic polymerization of cinnamal fluorene after a survey had been made of the effect of a large number of reagents on cinnamal fluorene in chloroform solution. Other polymerization agents less effective than antimony pentachloride were: BCl_3,[13] $TiCl_4$, $SnCl_4$,[14] WCl_6, $MoCl_5$, $FeBr_3$, halides of aluminum, Na, K, CrO_2Cl_2, $SeOCl_2$. A slight action was exerted by P_2O_5 and $FeCl_3$. Of substances lacking in polymerizing action may be mentioned: H_2SO_4, $SbCl_3$, $AsCl_3$, $SiCl_4$, Na_2O_2, BaO_2, benzoyl peroxide, $TiCl_3$, BBr_3, $SnCl_2$, SnI_4, chlorides of Hg, Cu, Cd, Pb, Bi, Zn, Ni, Co.

Cinnamal Indene

This compound was prepared by the following procedure, which gave better yields and was more expeditious than the procedure originally described by Thiele.[15] To a solution of 10.4 g. of cinnamic aldehyde and 14.4 g. of pure indene in 40 cc. of methyl alcohol, 8.5 cc. of a 30% solution of potassium hydroxide in methyl alcohol was added and, after the solution had stood for fifteen minutes, the separated reddish crystals, consisting of cinnamal indene and hydroxycinnamyl cinnamal indene, were filtered off. By recrystallization from ethyl acetate, cinnamal indene (9 g.) was obtained as reddish-yellow needles melting at 190°. The mother liquor was evaporated and the residue taken up in 150 cc. of hot benzene. On cooling, fine yellow needles of hydroxycinnamyl cinnamal indene came out, the more soluble reddish cinnamal indene remaining in the mother liquor. The product was purified by recrystallization from hot benzene; m. p., 160–161°.

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[13] This gave a polymer melting at 195–196°.

[14] This was used (in the case of anethole) by Gerhardt as far back as 1845 (*J. prakt. Chem.*, **36** (I), 270).

[15] Thiele, *Ber.*, **33**, 3398 (1900).

Thermo-polymerization.—Cinnamal indene was heated in a sealed tube at 200° for three days. The red, brittle resin thus obtained was dissolved in benzene and precipitated with alcohol. (Unpolymerized cinnamal indene is not thrown out by alcohol from benzene.) After drying *in vacuo*, the polymeric product thus obtained consisted of a dark yellow powder; m. p. 266–268°; mol. wt., 1692; C, 93.80; H, 6.08 (calcd. for $(C_{18}H_{14})_7$: 1610, 93.91, 6.09). The material was separated into four fractions by precipitation with absolute alcohol from benzene solution. The fractions gave the following results.

TABLE V

FRACTIONATION OF POLYCINNAMAL INDENE

Fraction	1	2	3	4
M. p., °C.	273–275	266–268	260–262	245–246
Mol. wt.	1892	1698	1534	1123

Polymerization by Stannic Chloride.—$SbCl_5$ was found to react with cinnamal indene so vigorously that it was difficult to avoid charring; hence $SnCl_4$, the action of which was not so vigorous, was used as a polymerization catalyst. To a solution of 4.5 g. of cinnamal indene in 75 cc. of chloroform was added 1.5 cc. of a 20% solution of $SnCl_4$ in chloroform and after the solution, which became dark red, had stood for two hours it was poured into 100 cc. of absolute alcohol. The precipitated polymer was purified by solution three times in chloroform followed by precipitation with alcohol; yield, 4.2 g. of a dark yellow powder; m. p. 238–242°; mol. wt., 972 (calcd. for $(C_{18}H_{14})_4$: 920).

Benzal Indene

Thermo-polymerization.—Benzal indene was heated at 178° in a sealed tube for five days. The red resin thus obtained was, unlike unpolymerized benzal indene, insoluble in alcohol. After purification by the precipitation of its (red) solution in xylene with alcohol, it was obtained as an orange-colored powder, m. p. 238–242°; mol. wt., 789; C, 93.95; H, 5.80 (calcd. for $(C_{16}H_{12})_4$: 816, 94.12, 5.88.).

Polymerization by Antimony Pentachloride.—To a solution of 3 g. of benzal indene in 60 cc. of chloroform was added 0.75 cc. of a 20% solution of $SbCl_5$ in chloroform and, after standing for half an hour, the deep blue solution was poured into 100 cc. of absolute alcohol. The precipitated polymer was purified by solution several times in benzene and precipitation with alcohol and was dried *in vacuo;* yield, 2.6 g. of a yellow powder; m. p., 252–255°; mol. wt., 1174 (calcd. for $(C_{16}H_{12})_6$: 1224).

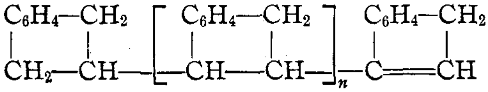
Hydroxybenzyl Benzal Indene

This compound was prepared by the following modification of the procedure described by Thiele.[15] To a mixture of 9 g. of pure indene and 16.5 g. of benzaldehyde cooled in a bath at 10° was added, drop by drop and with constant stirring, a solution of 0.5 g. of sodium in 20 cc. alcohol. After standing for two hours, the product which had separated was filtered off and washed, first with a little alcohol and then with water; yield, 17 g.; m. p. (from alcohol) 135–136°. From the mother liquor were obtained 1.5 g. of benzal indene (m. p., 88–89°) and a mixture of the two compounds melting at 120°. Polymerization was brought about by the addition of $SbCl_5$ to a chloroform solution, as in previous cases. After purification by precipitation three times by alcohol from a chloroform solution, the polymer was obtained in 95% yield as a deep yellow powder; m. p. 297–300°; mol. wt., 1928 (calcd. for $(C_{23}H_{18}O)_6$: 1860). The material gave red, non-colloidal solutions in most organic solvents but was insoluble in alcohol and in ether. $SnCl_4$ polymerized hydroxybenzyl benzal indene more slowly than did $SbCl_5$ and gave a lower polymeric product (m. p. 195–200°).

Summary

Indene is converted into high polymers by the catalytic action of antimony pentachloride and stannic chloride. The products are heterogeneous. The highest polymer isolated was represented by a fraction with a molecular weight corresponding to $(C_9H_8)_{29}$. The polymeric products obtained by heating indene are lower, the higher the temperature used. These products, too, are heterogeneous. There is a clear relationship between the melting point and molecular weight of polymers of indene.

All of the polyindenes, no matter what their molecular weight, contain one double bond per molecule. It is concluded that the polymerization of indene proceeds step-wise by the addition, involving the wandering of hydrogen, of successive molecules of the monomer, leading to products of the formula



$$\mathrm{\begin{matrix}C_6H_4{-}CH_2\\ |\qquad\quad|\\ CH_2{-}CH{-}\end{matrix}\left[\begin{matrix}C_6H_4{-}CH_2\\ |\qquad\quad|\\ {-}CH{-}CH{-}\end{matrix}\right]_n\begin{matrix}C_6H_4{-}CH_2\\ |\qquad\quad|\\ {-}C{=}CH\end{matrix}}$$

Cinnamal fluorene yields high polymers when treated with antimony pentachloride or stannic chloride, the products being mixtures. Heating at 240–250° also causes it to polymerize. Cinnamal indene and benzal indene also can be polymerized by heat and by catalysts. Hydroxybenzyl benzal indene can be polymerized by antimony pentachloride.

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THE PREPARATION OF THE SULFONYLIDES OF CRESOL- AND CHLOROPHENOL DISULFONIC ACIDS

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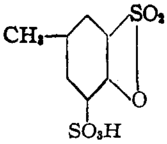
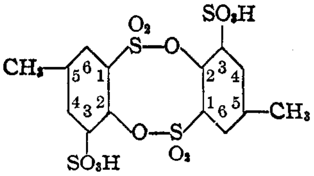
Raschig[1] found that *p*-cresol disulfonic acid was dehydrated by treatment with fuming sulfuric acid to give a product which was supposedly the monomolecular (*p*-cresol sulfone)-sulfonic acid (I).



(I)



(II)

In a very brief description of this compound, the fact was mentioned that it gave insoluble sodium and potassium salts which might be of value in analytical chemistry. Later,[2] Raschig concluded that his product was a disulfonic acid of *p*-methylphenylene-*o*-sulfonylide or, as it will

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[1] Raschig, *Z. angew. Chem.*, **25**, 1944 (1912); *Chem. Zeit.*, **36**, 1070 (1912).

[2] See Anschütz, *Ann.*, **415**, 65 (1918).