TABLE I

3-ARYLHYDRAZONOTRIACETIC LACTONES

Aryl	Color	M.p., °C.	Yield, %	Recrys.[a] from	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Phenyl	Rusty orange	193[b]	87	B				
o-Toluyl	Orange	217	90	B	11.47[c]	11.63[c]		
p-Biphenyl	Yellow-orange	281	93.5	B	70.58	70.75	4.61	4.66
2-Methyl-4-nitrophenyl	Yellow fibrous	255	93	B	54.18	54.07	3.83	3.61
2,4-Diiodo-6-carboxyphenyl	Brown	239	74.5	E,P[d]	49.25[e]	48.82[e]		
2,5-Dimethoxyphenyl	Red brown	185	55	B	57.93	58.14	4.86	4.76
m-Chlorophenyl	Yellow	233[f]	92.5	B	54.45	54.48	3.47	3.46
p-Chlorophenyl	Golden	248	96	B	54.45	54.78	3.47	3.52
o-Methoxyphenyl	Rust brown	193	84.5	E	59.99	60.01	4.65	4.77
p-Methoxyphenyl	Burned orange	199	92.5	B	59.99	60.26	4.65	4.68
1-Naphthyl	Rust brown	233	71.5	B	68.56		4.32	
2-Naphthyl	Orange	241[g]	85.7	E,G[h]	68.56	68.73	4.32	4.14

[a] B, benzene; E, ethyl acetate; P, petroleum ether; G, glacial acetic acid. [b] Obtained also from 3-bromotriacetic lactone (yield 50%). [c] Analysis for nitrogen. [d] A mixture of 3 parts ethyl acetate and 1 part petroleum ether, at −20° for one month. [e] Analysis for iodine. [f] Obtained also from 3-bromotriacetic lactone (yield 60%) and methylene bis-(triacetic lactone) (yield 80%). [g] Obtained also from 3-bromotriacetic lactone (yield 45%) and methylene bis-(triacetic lactone) (yield 70%). [h] A mixture of 2 parts glacial acetic acid and 8 parts ethyl acetate.

TABLE II

1-ARYL-3-CARBOXY-6-METHYL-4-PYRIDAZONES

Aryl group	M.p., °C.	Recrys.[a] from	Yield, %	Analyses[b] Calcd.	Analyses[b] Found
Phenyl[c]	173	W	80	N, 12.15	12.11
m-Chlorophenyl	193	EG	60	N, 10.60	10.51
o-Methoxyphenyl	170	EG	50	C, 59.99	60.00
				H, 4.65	4.65
2-Methyl-4-nitrophenyl	246	G	30	N, 14.53	14.39
p-Toluyl	154	EG	70	C, 63 92	64.03
				H, 4.95	4.87

[a] E, ethyl acetate; G, glacial acetic acid; W, water; EG, 50% glacial acetic acid and 50% ethyl ether. [b] C, carbon; H, hydrogen; N, nitrogen. [c] Neutralization equivalent 229, calcd. 230.

extracted with boiling petroleum ether. On cooling, the petroleum ether solution deposited 2.0 g. of white crystals, m.p. 89°. This product shows no depression of melting point when mixed with that obtained by the hydrochloride. The petroleum-ether-insoluble material (m.p. crude *ca.* 155–160°) was recrystallized from water to give a pure product, m.p. 188°, which showed no depression of melting point when mixed with triacetic lactone. The total yield of the 4-methoxy-6-methyl-2-pyrone, m.p. 89°, was 3.4 g., 60%.

Absorption Data.—The ultraviolet absorption measurements were made using 1.0-cm. silica cells and 95% ethanol solutions in a Beckman DU spectrophotometer. The infrared absorption measurements were made using potassium bromide pellets and a Baird double beam recording infrared spectrophotometer. 3-Phenylhydrazonotriacetic lactone shows absorption maxima at 248 mμ (log ε 1.33), 325 mμ (log ε 0.88) and 410 mμ (log ε 1.82).

LOUISVILLE 8, KY.

[CONTRIBUTION FROM THE CHEMICAL AND PHYSICAL RESEARCH LABORATORIES, THE FIRESTONE TIRE AND RUBBER CO.]

cis- and *trans*-Polyesters Formed by Condensation of Geometric Isomers of 2-Butene-1,4-diols and Ethene-1,2-dicarboxylic Acids

BY W. MAYO SMITH, JR.,[1] KENNETH C. EBERLY, ELMO E. HANSON AND JOHN L. BINDER

RECEIVED OCTOBER 24, 1954

Synthetic all-*cis* and all-*trans* polymers have not been reported. Low molecular weight polyesters of both *cis*- and *trans*-2-butene-1,4-diol with maleic and fumaric acid were synthesized and characterized. The monomers and polymers hydrogenate at significantly different rates. Only the all-*trans* polymer was crystalline by X-ray methods. The all-*cis* polymer was successfully crosslinked to give a clear film. No isomerization of the all-*cis* and all-*trans* polymers was indicated by chemical, X-ray and infrared analyses.

Introduction

Hevea and balata occur in nature in all-*cis* and all-*trans* configurations, respectively, but no exclusively *cis* or *trans* synthetic polymers were known. We have achieved the synthesis of such polymers.

In considering methods for the preparation of all-*cis* or all-*trans* polymers, we felt that ester interchange polyesterification offered the best possibility of success owing to the comparative mildness of such reactions over conventional esterification methods.

We therefore prepared pure *cis*- and *trans*-2-butene-1,4-diols and carried out their transesterification with methyl and ethyl maleate and fumarate, respectively. Diols of the highest possible purity are essential. The transesterification proceeded smoothly with methyl and ethyl maleate and with methyl fumarate in the presence of magnesium metal. Ethyl fumarate reacted sluggishly and required sodium as a catalyst. Identical *cis* or *trans* polymers resulted from either methyl or ethyl esters. Polymer yields were practically quantitative. At higher polymerization temperatures, insoluble cross-linked polymers resulted.

The all-*cis* and all-*trans* natures of the polymers

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[1] Presented in part at the 117th Meeting of the American Chemical Society in Detroit, Mich., April 18, 1950.

were clearly demonstrated by hydrolysis. Only the starting *cis* diol and maleic acid in the case of the *cis* polymer and only the starting *trans* diol and fumaric acid in the case of the *trans* polymer were obtained. High recoveries were obtained in each case. X-Ray, saponification and infrared studies confirmed these conclusions.

Experimental[2]

***cis*-2-Butene-1,4-diol.**—This was prepared by a modification of a patent issued to I. G. Farbenindustrie.[3] Starting with 5020 g. of 2-butyne-1,4-diol, distillation at 120° and 3-5 mm. gave 2236 g. of crude *cis*-2-butene-1,4-diol. Fractional distillation of this material at 115–30° at 1–5 mm. was made in a 42 cm. (19 mm. i.d.) column packed with $^1/_8$ in. glass helices at 20:1 reflux. The yield was 1570 g. (30.6%) of a light yellow crude *cis*-2-butene-1,4-diol, m.p. -1.5 to 1.2°.[4] The crude *cis*-diol (600 g.) and 800 g. of absolute methanol were stoppered in an Erlenmeyer flask and cooled to -70° for 21 hours. The crystals which deposited were filtered off and washed with cold methanol. The wet crystals were heated at 95° and 4 mm. for 2 hours to remove the methanol giving 163 g. of a colorless liquid. When cooled, this liquid crystallized sharply at 11.0°, b.p. 97.0° (2.3 mm.), d^{20}_4 (*in vacuo*) 1.0740, n^{20}_D 1.4793; molecular refraction obsd. 23.27, calcd. 23.25. Literature values reported are b.p. 132° (16 mm.), d^{20}_4 1.080 and n^{20}_D 1.478.[5] The b.p. is also given as 104–107° (0.7–0.8 mm.).[3] A mixture of 8.0 g. of pure *cis*-2-butene-1,4-diol (m.p. 11.0°) and 2.0 g. of pure *trans*-2-butene-1,4-diol (m.p. 27.3°) melted at 0° and indicated that the material sent Professor Marvel was approximately 80:20 *cis*:*trans* as reported.[4] The pure *cis*-diol failed to mass polymerize in 72 hours at 60–100° in the presence of benzoyl peroxide.

***trans*-2-Butene-1,4-diol.**—This was prepared from *trans*-1,4-dichloro-2-butene through the diacetoxy compound followed by hydrolysis and careful distillation as above. This *trans*-diol is a colorless, crystalline, water-soluble solid, b.p. 108.0° (3.8 mm.), m.p. 27.3°, d^{20}_4 1.0685 (supercooled), n^{20}_D 1.4779 (supercooled) and molecular refraction observed 23.34, calculated 23.25. Literature values reported are b.p. 131.5° (12 mm.), m.p. 25.0°, d^{20}_4 1.0687 (supercooled) and n^{21}_D 1.4772 (supercooled).[6]

Polymer Preparation: All-*trans* Polymer.—Diethyl fumarate 137.6 g. (0.80 mole) and *trans*-2-butene-1,4-diol (70.4 g., 0.80 mole) were treated under nitrogen with small pieces of freshly cut sodium (0.4 g.). The mixture became clear yellow almost immediately, becoming a clear orange after one hour at 45–58°. The temperature was then gradually raised and the pressure lowered to remove the alcohol formed by distillation; the final temperature and pressure reached were 116° and 1 mm. The total heating time was 73 hours, 60 of which were at 116° and 1 mm. The alcohol collected was about 80% of theory. The polymer when cooled to room temperature was very viscous and became an opaque yellow. The intrinsic viscosity of the polymer in cyclohexanone at 25° was 0.094. Its specific gravity was d^{25}_{25} 1.246, and its molecular weight (Rast) was 837.[7] A portion of the polymer was dissolved in acetone and diluted with ether until turbid. Cooling deposited approximately 0.1% of a finely crystalline white powder, m.p. 103.1–105.2°. This material is insoluble in benzene, limitedly soluble in boiling nitrobenzene (some fine gel deposits on cooling) and is sparingly soluble in molten camphor with decomposition. *Anal.* Found: C, 53.29, 53.18; H, 5.04, 4.87. Calcd. for the normal polymer unit: C, 57.14; H, 4.79.

All-*cis* Polymer.—*cis*-2-Butene-1,4-diol 176.0 g. (2 moles) and maleic acid 232.0 g. (2 moles) were allowed to react under conditions similar to those for the all-*trans* polymer. No catalyst was used initially. The melt temperature was kept for 5 hours at 55–95° after which the pressure was lowered to 100 mm. Most of the water of condensation was removed in the first two hours after which the pressure was lowered to 1 mm. and the mixture was held for 77 hours at 90–105°. The total heating time was 82 hours. The polymer was a clear amber color and had an intrinsic viscosity at 25° of 0.055. It was completely soluble in acetone. To 170 g. of this polymer was added 0.210 g. of brightly sanded magnesium ribbon. This mixture was heated at 105° and 1 mm. for an additional 47 hours. The catalyst was removed and washed with acetone. It had not lost weight. The polymer appeared identical to the material prior to the magnesium addition except that it was more viscous, its intrinsic viscosity at 25° now being 0.100. The Rast molecular weight was 663. Another preparation of intrinsic viscosity 0.176 had a Rast molecular weight of 1075.

A. **Mixed Polymers: *trans*-2-Butene-1,4-diol and Maleic Acid.**—One mole quantities of each were allowed to react in the presence of 0.167 g. of magnesium ribbon. The temperature was raised to 90° in one hour and, although some maleic acid remained solid, the pressure was reduced to 100 mm. After 6 hours, the pressure was reduced further to 0.5–1 mm. and the temperature was raised to 100–103°. The total heating time was 244 hours. The polymer was a clear light yellow which remained clear on cooling. The tacky polymer would not flow at room temperature and had an intrinsic viscosity at 25° of 0.087 and a Rast molecular weight of 826.

B. ***cis*-2-Butene-1,4-diol and Diethyl Fumarate.**—One molar quantities of each with 0.210 g. of magnesium ribbon were heated at 90° for 25 hours without visible evidence of reaction, as lowering of the pressure to 100 mm. failed to remove any alcohol. The magnesium was removed and chips of freshly cut sodium (0.315 g.) were added at 90°. The mixture immediately became a clear yellow-orange. At 100 mm. pressure, alcohol distilled rapidly and was recovered to the extent of 83% of theory in 2 hours. Forty-six hours after the sodium addition and at a temperature of 92–95° at 1 mm. pressure a sample sufficient for viscosity determination was withdrawn. The intrinsic viscosity at 25° was 0.051 and the Rast molecular weight was 710. Further heating at 97–99° and 0.2–0.5 mm. for 120 hours resulted in no increase in viscosity. The total heating time after the sodium addition was 166 hours. The clear yellow-orange, tacky polymer did not cloud on standing.

Saponification of the All-*cis* and All-*trans* Polymers.—The all-*cis* polymer (27.58 g.) was partially dissolved in 250 ml. of absolute alcohol. To this was added 15 g. of sodium hydroxide in 90 g. of distilled water. The polymer dissolved under reflux, which was maintained for 3 hours on a steam-bath, some solid separating from solution. The mixture was neutralized with dilute sulfuric acid to a *p*H of 5.0, and the precipitate, which was mostly sodium sulfate, filtered and washed three times in a Waring blendor with absolute alcohol. The combined filtrates were concentrated on a steam-bath to a small volume with subsequent separation of five crystalline fractions, each of m.p. 129.5–130.5°. The total recovery of maleic acid was 15.20 g. (97.2% of theory). Removal of the residual alcohol at aspirator pressure followed by a semi-micro distillation at 0.2 mm. yielded *cis*-2-butene-1,4-diol (86%), m.p. 10.8–11.0°, n^{20}_D 1.4793.

The all-*trans* polymer (10.02 g.) was hydrolyzed similarly. This polymer is considerably less soluble than the all-*cis* and required approximately 500 ml. of absolute alcohol for solution. To this was added 8 g. of sodium hydroxide in 50 ml. of distilled water. The total recovery of readily crystallized acid was 5.67 g. (99.6%), m.p. 288–290° (sublimes). Distillation at 0.5 mm. of the mother liquor gave *trans*-2-butene-1,4-diol, 81% recovery, m.p. 26.2–27.3°, n^{20}_D 1.4782.

Hydrogenation of Monomers and Polymers.—Acetone was used as a solvent for all hydrogenations except those of maleic and fumaric acids whose solubilities required the use of absolute alcohol. All hydrogenations were conducted at 25° and at 4 atm. pressure in 200 ml. of solvent in the presence of 0.100 g. of platinum oxide catalyst. The amounts of polymers hydrogenated were 0.1 mole, while 0.2 mole of the diols and acids were used. The theoretical hydrogen uptake was observed in all hydrogenations plus a small ex-

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[2] All melting points and boiling points are corrected.

[3] I. G. Farbenindustrie, British Patent 508,543; *Chem. Zentr.*, **II 110**, 3192 (1939).

[4] A sample of this practical material was sent to Prof. C. S. Marvel at the University of Illinois for use by the Office of Rubber Reserve. Marvel reports in C. R. 2289, 84th Progress Report on Synthetic Rubber Project, Feb. 10, 1950, that infrared study shows approximately 80% *cis* and 20% *trans* product present.

[5] A. Valette, *Ann. chim.*, [12] **3**, 644 (1948).

[6] C. Prevost, *Compt. rend.*, **183**, 1293 (1926).

[7] Molecular weights could not be obtained by the cryoscopic freezing point method due to the limited solubility of the polymers in the required solvents.

cess due to some slight reduction of the acetone solvent. An acceptable linear relationship was found when $\log p^\circ/p$ was plotted against t, where p° is the initial absolute hydrogen pressure and p is the absolute hydrogen pressure after time t in minutes.[8] The equations are then $\log p^\circ/p = kt$, and the rate of reaction $k = 2.303\ k\,V/\text{catalyst weight}$ in g., where V is the volume in liters. The *cis*- and *trans*-2-butene-1,4-diols hydrogenate at about the same rates, 51.8 and 46.8×10^{-2} liter min.$^{-1}$. Maleic and fumaric acids rates are quite different, maleic acid being 14.35×10^{-2} and fumaric 2.00×10^{-2}. The all-*cis* polymer had a k value of 18.96×10^{-2} and the all-*trans* 4.86×10^{-2} (Fig. 1).

Figure 1

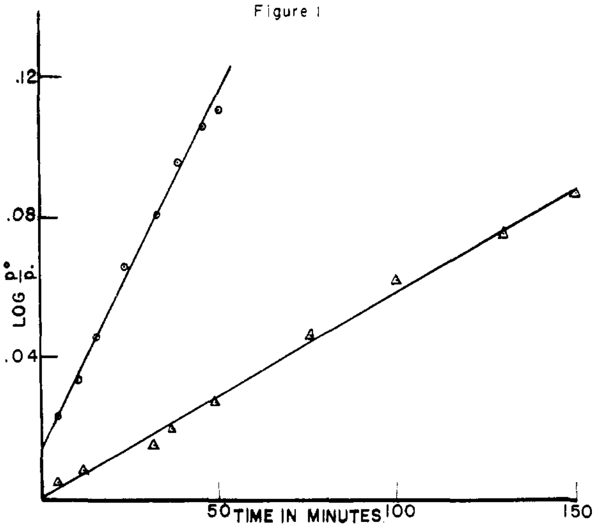

Fig. 1.—Hydrogenation: △, all-*trans* polymer, $k = 4.86 \times 10^{-2}$; ⊙, all-*cis* polymer, $k = 18.96 \times 10^{-2}$.

The hydrogenation rates for the polymer of the *cis*-diol and fumaric acid are given (Fig. 2). The values 4.14 and 1.89×10^{-2} represent the second step of the hydrogenation and the difference between these values may be due to experimental error, although a subsequent hydrogenation was similar. After 62 minutes and exactly 0.56 atm. hydrogen absorbed (one-half of theory), the hydrogenation rate decreases from 9.82 to 4.14×10^{-2}. In a subsequent hydrogenation of this same polymer, this sharp break occurred at one-half the theoretical hydrogen uptake. Saponification, as before, showed the acid fraction to be entirely fumaric; no succinic acid was obtained. This shows that the *cis*-diol was hydrogenating until the time of the saponification and that the hydrogenation of the *trans* part of the polymer, if at all, was very slight. In a mixed polymer of maleic acid and the *trans*-diol, the k values were 0.85×10^{-2} and 11.3×10^{-2} (Fig. 3). The first value on the slower rate curve after 40 minutes hydrogenation also was one-half of the theoretical absorption and, when saponified at this stage of the hydrogenation, gave in the acid product obtained all succinic acid and no maleic. Therefore, the *trans* part of the polymer has not hydrogenated until the *cis* is saturated, even though the hydrogenation rate of the *trans*-diol monomer is three times that of maleic acid.

Figure 2

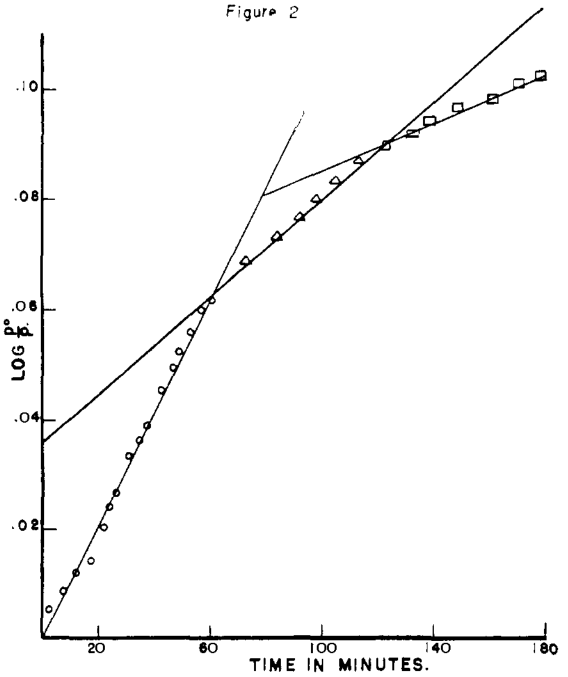

Fig. 2.—Hydrogenation of polymer of diethyl fumarate and *cis*-1,4-dihydroxy-2-butene: O, $k = 9.82 \times 10^{-2}$; △, $k = 4.14 \times 10^{-2}$; □, $k = 1.89 \times 10^{-2}$.

Figure 3

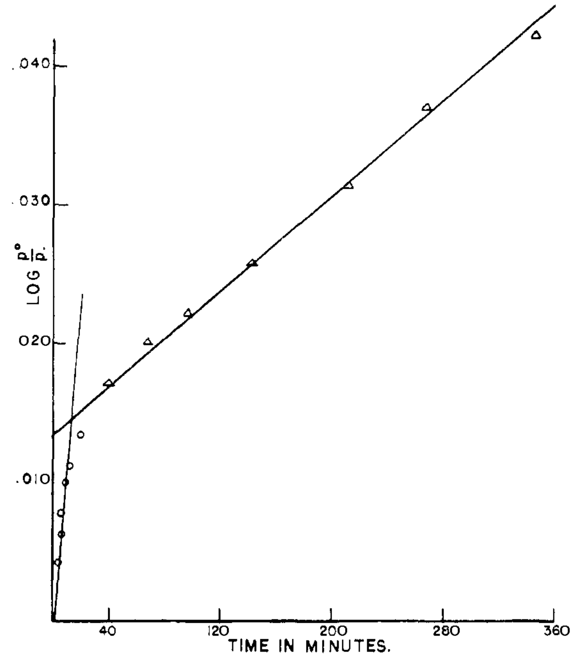

Fig. 3.—Polymer of maleic acid and *trans*-1,4-dihydroxy-2-butene: △, $k = 0.85 \times 10^{-2}$; O, $k = 11.3 \times 10^{-2}$.

Curing of Cast Films.—The all-*cis* polymer was dissolved in acetone containing 2% benzoyl peroxide based on the resin weight. The solution was concentrated until viscous on a steam-bath and then poured on a glass-plate treated with a mold release agent. The material would not cure in 40 hours at 50° but 15 minutes at 100° gave a clear film which was soft and flexible. This film could be stretched about 40% at break and remained water-white upon exposure under an ultraviolet lamp (S_1), but became brittle in about 1.5 hours. The film was not crystalline by X-ray methods.

The all-*trans* polymer treated similarly cured much slower requiring about 3 hours at 100°. This film was orange and opaque and of low strength. It embrittled in light and heat more rapidly than the all-*cis* polymer. The all-*trans* polymer has a crystalline X-ray diagram. Efforts to vulcanize the all-*cis* polymer with up to 40 parts of sulfur per 100 parts of polymer were fruitless.

Discussion of X-Ray Diffraction Observations.—The X-ray diffraction photographs obtained from the all-*trans* polymers were powder patterns typical of polycrystalline substances having essentially no amorphous phase. The crystallite Bragg spacings are displayed in Table I. All efforts to orient the crystallites by stretching the heat-

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[8] J. F. Fuzek and H. A. Smith, This Journal, **70**, 3743 (1948).

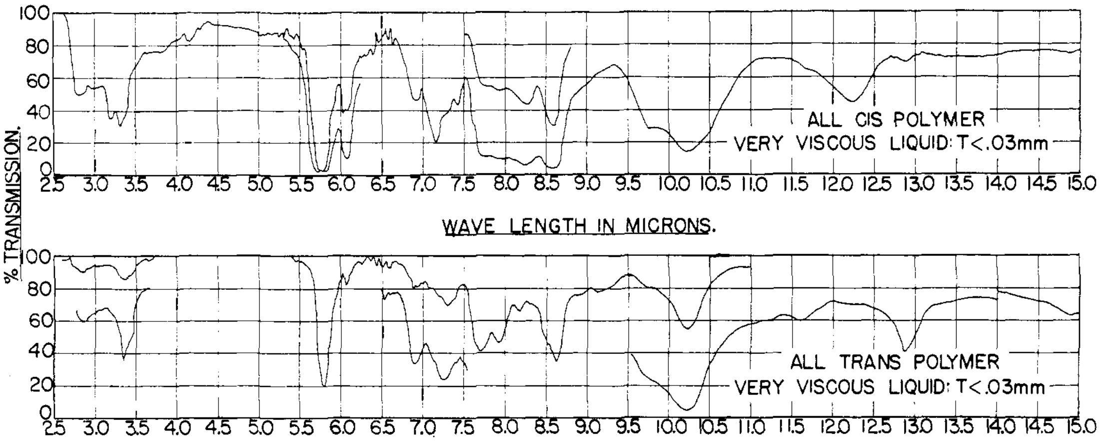

Fig. 4.

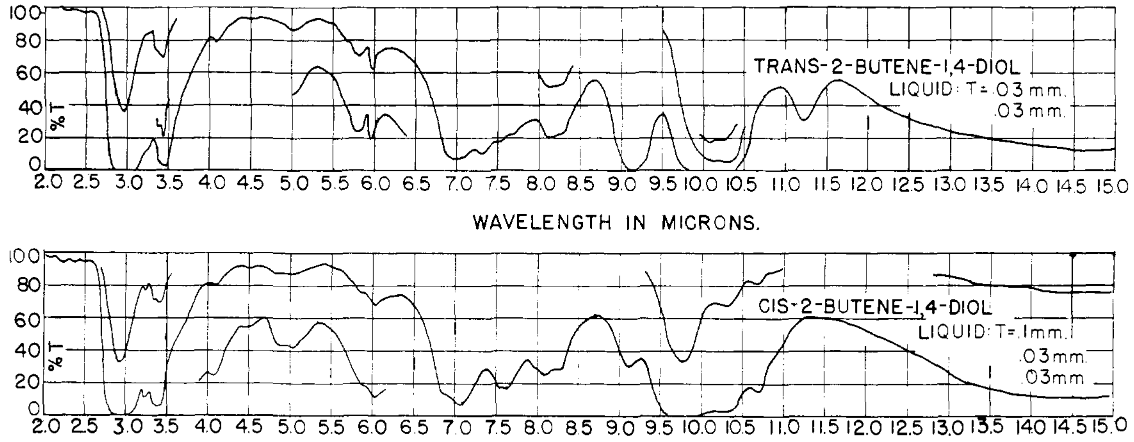

Fig. 5.

softened polymer failed, and therefore the chain identity period was not obtained.

TABLE I

X-RAY INTERPLANAR SPACINGS MEASURED FOR ALL-*trans* POLYMER

d-Value, Å.	Intensity	Remarks
9.1	Medium	Broad line
5.2	Very weak	Very sharp line
4.24	Strong	Broad
3.79	Strong	Very broad
3.16	Medium	Broad
2.60	Very, very weak	Possibly two lines because "line" is very broad

The X-ray diffraction patterns of the *cis* polymers consisted only of a diffuse halo which is typical of amorphous materials. Fibering was not induced by stretching, and exposures of the all-*cis* polymers to temperatures from 23 to −67° failed to produce any X-ray evidence for crystallinity.

It had been expected that the *cis*, as well as the *trans*, polymers would be crystalline because of their postulated regularity of structure. However, the following considerations clarified the apparent anomaly:

The model of the all-*trans* polymer chain was found to fall naturally into a planar zig-zag configuration with considerable latitude for rotation about the single bonds. Based on the published values[9] for the bond angles and distances, the identity period for the extended planar configuration was 11.6 Å. covering a span of the 2 constituent monomer units. Such a configuration would have a high probability for crystallization.

The all-*cis* polymer configuration, however, is complicated by severe steric hindrances to rotation about the single bonds. From a study of a Fischer model of the polymer it was concluded that the most regular configuration possible for the molecular chain would be a spiral with a rotation rate of not more than one revolution per 4 monomer units. The spiral configuration by itself would not rule out the possibility of crystallization except for the fact that both left- and right-handed spirals are likely to be present in the same and in different molecules. During polymerization, as each new chemical unit is added to the chain, the direction of spiralling may be continued or reversed. Since the poly-

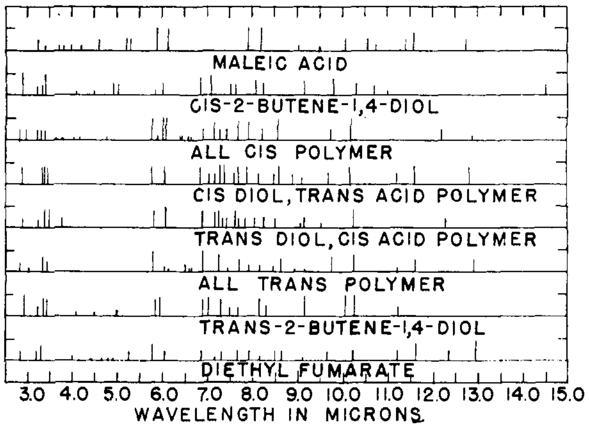

Fig. 6.

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[9] H. Mark, "High Polymers," Interscience Publishers, Inc., New York, N. Y., 1940, Vol. II, pp. 15, 16; 1941, Vol. III, pp. 8, 10, 12 and 14.

mers have a molecular weight of about 1000, or 6 complete chemical units, there are therefore 6 different points in the chain where a new spiral direction may be introduced. On a purely statistical basis, therefore, there are 64 different configurations possible for the *cis* molecule. After a *cis* molecule is formed, the direction of the spiral cannot be changed because of steric hindrances. Therefore, it appears extremely unlikely that crystallization would take place in the all-*cis* polymer.

Crystallization was not observed by the X-ray diffraction technique for any of the *cis–trans* polymers. On the basis of the above analysis for all-*cis* molecules, and the irregularity introduced by the mixing of the *cis* and *trans* structures, crystallization would not be expected to occur.

The Infrared Spectra of Polymers.—The chemical evidence seems conclusive that the all-*cis* polymer and the all-*trans* polymer are completely *cis* and *trans*, respectively. Nevertheless, it seemed desirable to study the infrared spectra of these compounds not only to verify the deductions from chemical evidence but also to observe the spectra of such synthetic polymers. The spectra were obtained using a Beckman IR2 spectrophotometer. Those of the all-*cis* and all-*trans* polymers were obtained by point-by-point (sample-in, sample-out) measuring using a rock salt plate as standard and are shown in Fig. 4. The spectra of the pure diols were obtained in the same manner and are shown in Fig. 5. Those of the mixed polymers and monomers were obtained by recording and shown schematically in Fig. 6. The spectra of Figs. 4 and 5 are also included in this figure to facilitate comparison.

A comparison of the spectra of the mixed polymers with those of the all-*trans* and all-*cis* polymers shows many differences in the number of bands and intensities. These differences are large enough to show that, for example, there is no *cis*-diol–*trans* acid polymer or *trans* diol–*cis* acid polymer in the all-*cis* polymer. Thus if any isomerization occurred during the preparation of either the all-*cis* or all-*trans* polymer it must have happened in both the diol and the acid.

The question of whether or not both the diol and acid isomerized during the preparation of either the all-*cis* or all-*trans* polymer is more difficult to settle on the basis of the infrared spectra of the polymers. This is particularly true with respect to the presence of some all-*trans* polymer in the all-*cis* polymer. The C=C bands at 6.04 and 6.10 μ in the spectra of the all-*cis* polymer are sufficiently intense to make it improbable that there is much, if any, *cis* polymer in the all-*trans* polymer, especially since the band at 6.06 μ in the spectrum of the all-*trans* polymer is probably a harmonic of a lower lying band, as found by Rasmussen and Brattain[10] in the spectra of other *trans* compounds. Repeated experiments showed the 6.06 μ band to be real for this polymer and not due to water. The absence of it would be cause for concern as indicated above. The C=C bands at 6.04 and 6.10 μ, as well as the absence of any indication of a band at 12.25 μ in the all-*trans* polymer spectrum, seem sufficient to warrant the conclusion that the all-*trans* polymer is substantially, and probably completely, pure.

At first thought, it might seem that the well-established correlation rule of assigning the 10.34 μ band to a *trans* $\diagdown\text{CH}{=}\text{CH}\diagup$ structure would unambiguously determine whether any *trans* polymer is present in the *cis* polymer. Unfortunately, both of the *cis* monomers used here have bands in their spectra at or near this wave length. A comparison of the spectra of the two polymers shows that, except for the 12.9 μ band in the all-*trans* polymer spectrum, it would be difficult, if not impossible, to detect a small amount (5%) of the *trans* polymer in the *cis* polymer in this manner. There is a weak band in the spectrum of the all-*cis* polymer which might indicate the presence of some all-*trans* polymer. If so, the amount must be small since, otherwise, the band at about 8.6 μ in the all-*cis* polymer spectrum would be broader than found, due to the shape of the 8.6 μ band in the all-*trans* spectrum. However, except for this band, the spectrum given can be regarded as the spectrum of an all-*cis* polymer of maleic acid and *cis*-2-butene-1,4-diol.

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(10) R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 120 (1947).

AKRON 17, OHIO

[CONTRIBUTION FROM HERCULES EXPERIMENT STATION, HERCULES POWDER CO.]

The Autoxidation and Chromic Anhydride Oxidation of the Lactone of "Hydroxytetrahydroabietic Acid"[1]

BY JAMES MINN, THOMAS F. SANDERSON AND LEE A. SUBLUSKEY

RECEIVED SEPTEMBER 6, 1955

The lactone of "hydroxytetrahydroabietic acid" in a molten state has been found to undergo non-catalytic and catalytic autoxidation with pure oxygen. In the products isolated—hydroperoxides, alcohols and ketones—the basic tricyclic ring structure of the original lactone was preserved; the oxidative attack was limited to the vicinity of the 7-isopropyl group. Similar results were also obtained with an anhydrous chromic anhydride oxidation of the lactone. The structures of the various products were established by interconversions with one another and by a conversion to the known pimanthrene.

Although considerable attention has been given to the autoxidation of relatively simple, saturated monocyclic and bicyclic hydrocarbons, such as substituted cyclopentanes and cyclohexanes, pinane and the decalins,[2] studies with larger polycyclic structures have not been reported. In this paper we describe the autoxidation of a tricyclic diterpenoid, the lactone of "hydroxytetrahydroabietic acid." This compound, m.p. 131–132°, whose structure recently has been shown to be 4aα-hydroxy-1β,4bβ-dimethyl-7ξ-isopropyl-8aα,10aβ-perhydrophenanthrene-1α-carboxylic lactone (I),[3] is the product which is so readily obtained from commercial, partially hydrogenated rosin[4] when treated with strong mineral acid.[5]

The lactone I, when stirred at a few degrees above its melting point in an atmosphere of oxygen with an ultraviolet light initiating source, was found to absorb oxygen readily, and in a few hours produced a reaction mixture which had an active oxygen content of 1.0%. By countercurrent distribution be-

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(1) Presented before the Division of Organic Chemistry, 128th Meeting, Am. Chem. Soc., Minneapolis, Minn., September 15, 1955.

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