Summary

Two isomers of 2-methyl-1-indanol have been prepared. One of these, which we believe to be the *cis*-isomer, was obtained by the room temperature hydrogenation of 2-methyl-1-indanone over Raney nickel. The other, which we believe to be the *trans*-isomer, was obtained by hydrogenation of the same ketone at 130° over copper chromium oxide.

A study of the thermal decomposition of *cis*-2-methyl-1-indanyl acetate and methyl *cis*-2-methyl-1-indanylxanthate has revealed that these compounds are much more stable than the corresponding *trans*-isomers. Decomposition of all of the esters led to 2-methylindene. These results indicate that while a cyclic transition state complex[3,4,5] is probably the preferred intermediate in these reactions, there must be another reaction path by which elimination can occur.

URBANA, ILLINOIS RECEIVED AUGUST 3, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Intermolecular and Intramolecular Cross-Linking in Concentrated Polymer Solutions

BY DAVID B. FORDYCE[1] AND JOHN D. FERRY

In a number of qualitative studies,[2-4] linear polymer molecules in solution have been cross-linked by chemical reactions to form branched structures and three-dimensional networks. Although the formation of cross bonds was obvious from changes in physical properties and eventual gelation, no information was provided in these earlier investigations concerning the actual number of linkages introduced. The only quantitative studies of the effects of a known number of cross-links on physical properties have been those recently reported by Flory[5] on rubber vulcanized by disazodicarboxylates, in the undiluted state.

In theoretical treatments of the statistics of cross-linking,[6,7] formation of cyclic structures has not been taken into account; in the application of these theories to the linkage of long linear molecules, it must be assumed that each bond is intermolecular, joining two reactive groups on different molecules. It is recognized that some intramolecular bonds are formed, which do not contribute to building up a three-dimensional network, and that the proportion of such intramolecular bonds should be greater if the cross-linking takes place in the presence of an inert diluent. However, there has been no experimental information concerning the actual proportions of intermolecular and intramolecular links.

The present paper describes the introduction of a stoichiometrically known number of cross-links into a solution of linear polymer molecules by quantitative reaction with a cross-linking agent. Since each intermolecular link diminishes the number of molecules by one, while each intramolecular link leaves the number of molecules unchanged, the proportion of intermolecular links can be calculated from the change in number-average molecular weight, and the proportion of intramolecular links found by difference. The quantity of cross-linking agent employed is sufficiently small so the gel point is not reached.

After preliminary trials with various systems, we chose the reaction between a 1:1 copolymer of styrene and maleic anhydride as the initial linear molecule and a glycol or diamine as the cross-linking agent. This reaction is simple and would be expected to be quantitative. The only solvent found to be suitable was dioxane, which is inert with respect to both polymer and cross-linking agents, and has a dielectric constant sufficiently low so that any occasional hydrolyzed anhydride groups on the polymer remain un-ionized and the complications exhibited by polyelectrolytes with respect to osmotic pressure and viscosity in dilute solution are avoided. Experiments with cross-linking by hexamethylene glycol and benzidine are presented here. Other experiments with hexamethylenediamine gave qualitatively similar results, but are not reported because in this case the reaction was so rapid that it is doubtful whether a homogeneous mixture was achieved before the cross-linking process commenced.

Materials and Methods

The copolymer of styrene and maleic anhydride (SYHM. Blend 1) was furnished by Union Carbide and Carbon Corporation.[8] It was dissolved in methyl ethyl ketone and fractionated roughly by precipitation with benzene. The first two fractions, A and B, comprising 31 and 29%, respectively, of the original material, were used for cross-linking by benzidine and hexamethylene glycol, respectively. These two cuts did not differ greatly in number-average molecular weight, suggesting that the original material was relatively homogeneous. The fractions were dried by aspiration followed by heating *in vacuo* at 65° for 60 to 70 hours. Although the portions used for cross-linking experiments were not heated above 65° for fear of possible degradation, aliquots heated to 100° *in vacuo* showed a small additional weight loss, and concentrations of solutions made up by weight were expressed in terms of this fully dried material.

Hexamethylene glycol (m. p. 38-41°) was obtained from E. I. du Pont de Nemours and Co., and benzidine (m.p. 127-128°) from H. Rubin.[9] The benzidine was kept under nitrogen. Solutions of the glycol and benzidine were prepared immediately before use. Dioxane was purified by refluxing with hydrochloric acid, neutralization, refluxing

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(1) Carbide and Carbon Chemicals Fellow in Physical Chemistry, 1949-1950. Rohm and Haas Co., Philadelphia, Pa.

(2) W. E. Gloor and H. M. Spurlin, THIS JOURNAL, **58**, 854 (1936).

(3) R. Signer and P. von Tavel, *Helv. Chim. Acta*, **26**, 1972 (1943).

(4) I. Jullander, *Ark. Kemi Mineral. Geol.*, **21A**, No. 8 (1945).

(5) P. J. Flory, N. Rabjohn and M. Shaffer, *J. Polymer Sci.*, **4**, 225, 435 (1949).

(6) P. J. Flory, THIS JOURNAL, **63**, 3083, 3091, 3096 (1941); **69**, 30 (1947).

(7) W. H. Stockmayer, in "High Polymers," edited by S. B. Twiss, Reinhold Publishing Co., New York, N. Y., 1945, p. 61.

(8) We are indebted to Mr. G. M. Powell, Carbide and Carbon Chemicals Division, for this material.

(9) 29 W. 15th St., New York, N. Y.

with sodium, and distillation through a 30-plate Oldershaw column. Pyridine was dehydrated over barium oxide and distilled through the Oldershaw column.

Cross-Linking Procedure.—The proper weights of a stock solution of polymer in dioxane (about 25%), a dilute solution of cross-linking agent in dioxane, and additional dioxane as diluent were added to a mixing flask equipped with a mercury seal stirrer and thoroughly mixed at room temperature to give a system with the required values of weight fraction of polymer (w_2) and equivalence ratio of cross-linking agent to anhydride groups (ρ_T). In the hexamethylene glycol experiments the system contained 5% of pyridine also, as a catalyst for the alcoholysis reaction. The mixture was transferred to another flask with two reflux condensers, through one of which passed a stirrer closed by a mercury seal, while the other could be opened for withdrawal of samples; in the benzidine experiments, the system was swept with nitrogen before closing. The mixture was then maintained at an elevated temperature, and samples were withdrawn at intervals and diluted to 0.30% polymer for determination of specific viscosity. When the specific viscosity had attained a constant value, the reaction was assumed to be complete and the mixture was cooled and diluted to a concentration of about 2% polymer to give a stock solution for measurements of osmotic pressure and intrinsic viscosity. The concentration of the stock solution was determined by a dry weight based on heating at 110° *in vacuo* for 125 hours.

Osmotic Pressure Measurements.—Osmotic pressures (π) were determined at 25° in a stainless steel osmometer of the Flory type[10] with a cellophane membrane. Each original and cross-linked sample was measured at several different concentrations and the number-average molecular weight ($\bar{M}_n$) and the usual constant μ were calculated from a plot of π/c against c with a linear extrapolation. The solutions of polymer cross-linked with hexamethylene glycol contained small amounts of pyridine, but this additional component soon diffused through the membrane and did not interfere with establishment of osmotic equilibrium.

Intrinsic Viscosity Measurements.—Viscosities of each sample at several different concentrations were measured at 25° by viscosimeters of the Ostwald or Ubbelohde type, and the intrinsic viscosities were obtained by the usual extrapolation methods. Kinetic energy corrections, which were estimated from the dimensions of the viscosimeters to be of the order of 1%, were neglected.

Results

Specification of Reaction Conditions.—A number of preliminary experiments were made to determine the best temperature and minimum time required for completion of each reaction. With hexamethylene glycol in the presence of 5% pyridine the specific viscosity approached a constant value after 60 hours at 60°; no significant degradation of the polymer occurred within this time interval, as shown by measurements in the absence of cross-linking agent (Fig. 1). With benzidine a constant value was approached after 15 hours at this temperature (Fig. 1). It was assumed that the reaction was then complete and that the stoichiometric ratio of added hydroxyl (or amino) groups to anhydride residues present, ρ_T, was equal to the fraction of anhydride residues which had reacted to form cross-links.[11]

Characterization of Cross-linked Samples.—Each of the two cross-linking agents was studied at two levels of total cross-linking, ρ_T, and several polymer concentrations. The available range of ρ_T was limited by trivial changes in molecular weight and viscosity on the low side and gelation on the high side. Table I gives the values of number-average molecular weight, μ, and intrinsic viscosity for each of the original and cross-linked samples. The fraction of anhydride residues which have reacted to form effective or *intermolecular* cross-links, ρ_E, is also given, calculated from the equation

$$\rho_E = (1 - \bar{M}_n^0/\bar{M}_n)(2M_0/\bar{M}_n^0) \qquad (1)$$

where $\bar{M}_n^0$ and $\bar{M}_n$ are the number-average molecular weights of the polymer before and after cross-

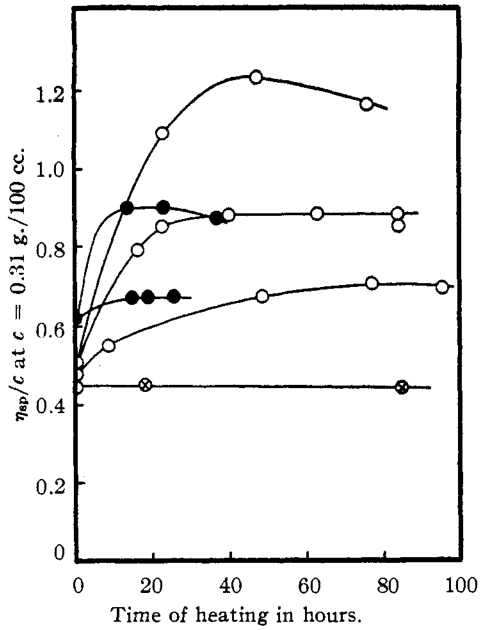

Fig. 1.—Reduced specific viscosity plotted against reaction time at 60°: ○, hexamethylene glycol, ρ_T = 0.70%, w_2 in descending order = 0.24, 0.20, 0.15; ●, benzidine, ρ_E = 0.40%, w_2 in descending order = 0.10, 0.05; ⊗, no cross-linking agent, w_2 = 0.10.

TABLE I

PROPERTIES OF CROSS-LINKED POLYMERS

ρ_T %	Heating time, hr.	w_2[a]	$\bar{M}_n \times 10^{-3}$	μ	$[\eta]$ (g./100 cc.)$^{-1}$	ρ_E %
			Hexamethylene glycol (fraction B)			
0	..	...	64.3	0.417	0.43	...
0.50	93	0.15	72.8	.413	.55	0.074
	67	.23	81.5	.420	.66	.132
	65	.238	85.2	.412	.69	.154
.70	95	.15	80.2	.417	.61	.124
	84	.20	87.3	.425	.71	.166
	77	.24	89.9	.435	.99	.179
			Benzidine (fraction A)			
0	..	...	73.0	0.423	0.52	...
0.30	15	0.05	76.6	.432	.56	0.026
	14	.10	93.7	.422	.64	.122
	13	.14	104.	.421	.69	.165
.40	26	.05	85.8	.424	.58	.082
	37	.10	97.8	.422	.78[b]	.140

[a] Weight fraction of polymer during reaction. [b] This value has been corrected for degradation during 16 days storage of the stock solution by multiplying by the ratio of ln η_r/c for the stock before and after storage (1.24).

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(10) G. V. Browning and J. D. Ferry, *J. Chem. Phys.*, **17**, 1107 (1949).

(11) The possibility that occasional hydrolyzed carboxyl groups, if present, might bind benzidine by so-called salt linkages was considered. It is believed that under the reaction conditions any such linkages would dissociate reversibly so that all the benzidine would eventually be consumed by anhydride groups to form permanent amide bonds.

linking, and M_0 is the molecular weight of a maleic anhydride plus a styrene residue (202). The factor 2 arises from the fact that two anhydride residues must react to form one cross-link.

The ratio of intermolecular to total cross-links, ρ_E/ρ_T, is plotted in Figs. 2 and 3 against the reciprocal of the volume fraction of polymer present during the cross-linking reaction. The latter values were calculated by assuming that the specific volumes of the solutions vary linearly on a weight fraction scale from that of the solvent to that of the pure polymer. As expected, the proportion of intermolecular or effective linkages falls off rapidly with increasing dilution, and the results are consistent with a ratio of unity at infinite concentration of polymer. The values of ρ_E/ρ_T do not appear to depend much on ρ_T within the rather narrow range covered.

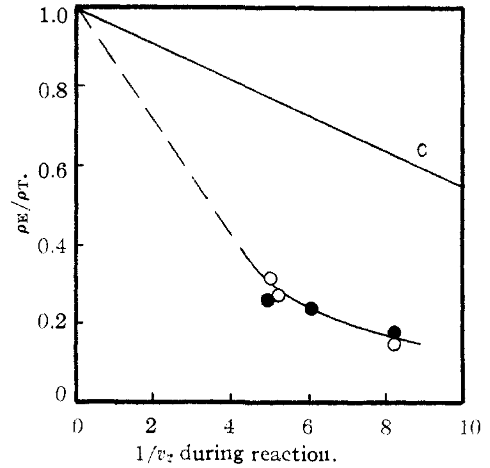

Fig. 2.—ρ_E/ρ_T plotted against reciprocal volume fraction of polymer during reaction, for samples cross-linked with hexamethylene glycol: ○, ρ_T = 0.50%; ●, ρ_T = 0.70%; C, calculated from intrinsic viscosity.

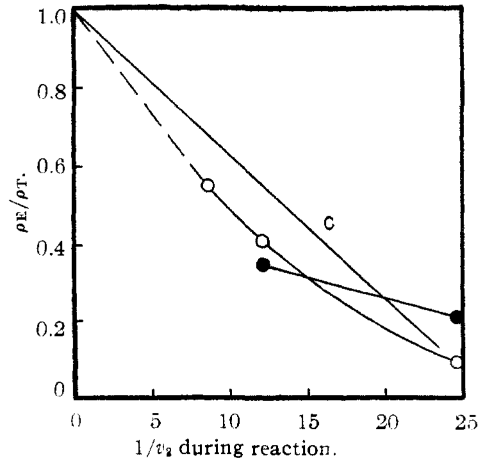

Fig. 3.—ρ_E/ρ_T plotted against reciprocal volume fraction of polymer during reaction, for samples cross-linked with benzidine: ○, ρ_T = 0.30%; ●, ρ_T = 0.40%; C, calculated from intrinsic viscosity.

Discussion

The decrease in ρ_E/ρ_T with increasing dilution can be given a rough but very simple theoretical interpretation. It is assumed that the domain of a single polymer coil can be approximately defined by a sphere within which the concentration of polymer segments is constant.[12] In a concentrated solution this domain is also pervaded by foreign molecules, and the sum of the volume fractions of native segments (v'_2) and foreign segments (v''_2) is taken to be the over-all volume fraction of polymer in the solution (v_2). Then if cross-linkage occurs at random the probability that any given link is intermolecular is v''_2/v_2. It follows that $\rho_E/\rho_T = 1 - v'_2/v_2$. If the volume of the spherical domain is independent of concentration, a plot such as Fig. 2 or 3 should be represented by a straight line of intercept unity and slope $-v'_2$.

To obtain an estimate of v'_2, we assume that the coil volume is the same as that in dilute solution, where it can be gaged by the intrinsic viscosity, applying the Einstein equation. Then[12] $v'_2 = 0.025/[\eta]\rho_2$, where ρ_2 is the density of the polymer (1.29). This yields values of 0.037 for Fraction A and 0.045 for Fraction B. It may be expected that the coil volume will be somewhat smaller in concentrated solution, however, than in very dilute solution where the intrinsic viscosity is measured, so these values probably represent lower limits for v'_2. Lines with the calculated slopes are drawn in Figs. 2 and 3. For benzidine there is rough agreement with the experimental data but for hexamethylene glycol the calculated slope is too small. The discrepancy in the latter case may be due to a tendency for the glycol hydroxyls to react with adjacent maleic anhydride residues on the polymer chain, giving a probability of intramolecular linkage somewhat in excess of that calculated on the basis of reaction at random. Such chelate linking would be more likely for hexamethylene glycol, whose reactive groups are separated by a flexible chain with an average length of about 5 Å., than for benzidine, whose reactive groups are separated by a rigid structure about 10 Å. long.

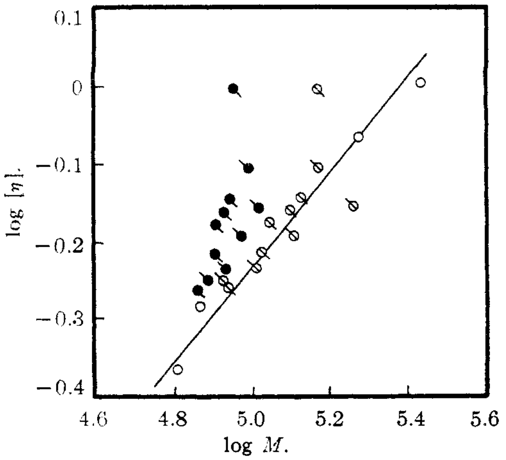

Fig. 4.—Logarithmic plot of intrinsic viscosity against molecular weight: ○, linear fractions; ●, cross-linked samples using measured number-average molecular weight; ⊖, cross-linked samples using estimated weight-average molecular weight. Downward tags hexamethylene glycol; upward tags benzidine.

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[12] P. J. Flory, *J. Chem. Phys.*, **13**, 453 (1945).

Intrinsic Viscosities.—The intrinsic viscosities of all samples are plotted against number-average molecular weight in Fig. 4, together with values for several other linear fractions from unpublished data. For the cross-linked samples, $[\eta]$ increases much faster than for the linear samples. This is primarily due to a distortion of the molecular weight distribution function and the fact that $[\eta]$ reflects an average which is closer to $\bar{M}_w$ than to $\bar{M}_n$. The weight average molecular weights of the cross-linked samples can be estimated by an equation due to Stockmayer,[13] which is in our notation $\bar{M}_w = \bar{M}_w{}^0/(1 - \rho_E\bar{M}_w{}^0/M_0)$, taking $M_w{}^0$ as approximately equal to $\bar{M}_n{}^0$. When the intrinsic viscosities are plotted against the estimated weight average molecular weights, the linear and cross-linked samples fall much closer together.

Values of μ.—The thermodynamic constant μ is expected to increase with cross-linking.[14,15] However, in our results this effect is barely perceptible (Table I).

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Summary

1. A copolymer of styrene and maleic anhydride has been cross-linked in concentrated dioxane solutions by hexamethylene glycol and by benzidine. The proportion of anhydride groups reacted, ρ_T, was calculated from the amount of cross-linking agent added, and the proportion reacted to form intermolecular linkages, ρ_E, was calculated from the change in number-average molecular weight.

2. The ratio ρ_E/ρ_T decreased with decreasing concentration of polymer during reaction. The data for benzidine were in rough agreement with an approximate theory based on estimating the volume pervaded by a single polymer coil from intrinsic viscosity. The data for hexamethylene glycol showed a deviation which is attributed to a tendency to chelate linkage on the polymer.

MADISON, WISCONSIN RECEIVED JUNE 21, 1950

[13] W. H. Stockmayer, *J. Chem. Phys.*, **12**, 125 (1944).

[14] P. M. Doty, M. Brownstein and W. J. Schlener, *J. Phys. Coll. Chem.*, **53**, 213 (1949).

[15] M. S. Muthana and H. Mark, *J. Polymer Sci.*, **4**, 527 (1949).

[A CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Mechanism of the Chromic Acid Oxidation of Isopropyl Alcohol. The Chromic Acid Ester[1]

BY FRANK HOLLOWAY, MERRILL COHEN AND F. H. WESTHEIMER

Introduction

A series of investigations[2,3,4,5] carried out over the past eleven years has suggested that the chromic acid oxidation of isopropyl alcohol takes place by way of an ester of chromic acid. In dilute acid, the proposed mechanism[1,5] is as follows

$$HCrO_4^- + CH_3CHOHCH_3 + H^+ \underset{}{\overset{\text{rapid}}{\rightleftarrows}} (CH_3)_2CHOCrO_3H + H_2O \quad (1)$$

$$B + (CH_3)_2CHOCrO_3H \xrightarrow[\text{determining}]{\text{rate}} BH^+ + (CH_3)_2CO + HCrO_3^- \quad (2)$$

Here the symbol B represents a molecule of water or of some other base. The scheme here outlined corresponds to the correct kinetics in dilute aqueous acid: the rate is first order in the acid chromate ion,[2] in alcohol[2] and in hydrogen ion. (In more concentrated acid solutions, the reaction rate is second order in hydrogen ion,[2] and the ester must be further protonated.) The mechanism of equations (1) and (2) also corresponds to the fact that the first unstable chromium intermediate is a compound of tetravalent chromium[3]; the subsequent reactions of the tetravalent chromium compound are discussed elsewhere.[3,5] Furthermore, the mechanism here advanced explains the fact[4] (determined from studies with $CH_3CDOHCH_3$) that the rate controlling step of the oxidation involves the cleavage of the C–H bond.

The data, here reported, consist of two parts. (I) A chromic acid ester of isopropyl alcohol can be prepared in benzene or toluene solution; in these solvents the ester is decomposed rapidly by bases (such as pyridine) to form acetone. (II) In aqueous solution (where the base, B, of equation (2) is generally water) the reaction is also catalyzed by pyridine. The relationship of these new facts to the mechanism represented by equations (1) and (2) is then discussed.

I. Chromic Acid Esters

Di-*t*-butyl chromate[6] and several analogous chromic acid esters[6,7] of tertiary alcohols have been prepared by Wienhaus and others. Wienhaus pointed out that when an aqueous solution of chromic acid and of a secondary alcohol was shaken with hexane or carbon tetrachloride, an unstable yellow compound was extracted into the non-aqueous layer. Presumably this was an ester of chromic acid and the secondary alcohol; the extreme ease with which the esters decompose in

[1] Presented in part at the 117th Meeting of the American Chemical Society, Detroit, April 19, 1950.

[2] F. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943).

[3] W. Watanabe and F. Westheimer, *ibid.*, **17**, 61 (1949).

[4] F. Westheimer and N. Nicolaides, THIS JOURNAL, **71**, 25 (1949).

[5] F. Westheimer, *Chem. Revs.*, **45**, 419 (1949); Errata, June, 1950.

[6] H. Wienhaus, *Ber.*, **47**, 322 (1914).

[7] W. Hückel and M. Blohm, *Ann.*, **502**, 114 (1933).