Reaction of Hydrogen Chloride–Aluminum Chloride with Toluene.—Excess toluene, 18.6 ± 0.1 mmoles, was placed in the sample tube and cooled to −84.1° (a solid–liquid slush of ethyl acetate was used). Measured amounts of hydrogen chloride were then introduced. After each addition, the equilibrium pressure in the system was noted. The data are given in Table I and define the line "without $AlCl_3$ at −84.1°" in Fig. 1. The contents of the tube were removed to storage and a small quantity of aluminum chloride, 0.36 ± 0.02 mmole as $AlCl_3$, was introduced into the reaction tube as described previously. The hydrogen chloride–toluene mixture was returned to the tube and the mixture maintained at −80° with intermittent stirring for 6 days. By this time practically all of the aluminum chloride had dissolved. (A few minute crystals adhered to the glass walls above the surface of the solvent; however, by visual observation this represented a negligible fraction of the aluminum chloride introduced.) The −84° bath was then raised and pressure readings taken until no change was observed. The equilibrium pressure in the presence of 6.62 mmoles of hydrogen chloride was 71.4–71.8 mm., considerably below the 76.6 mm. value obtained in the absence of aluminum chloride (Table I).

From the graphical representation of the data (Fig. 1), the decrease in pressure corresponds to a loss of hydrogen chloride of 0.38 mmole as compared to the 0.36 mmole of aluminum chloride introduced.

As indicated in Table I, the solution was a clear green in color. Removal of part of the hydrogen chloride caused a white solid (presumably aluminum chloride) to precipitate. Return of hydrogen chloride caused the aluminum chloride to dissolve, regenerating the green solution. Under these conditions decomposition of the complex is a relatively slow process. Thus removal of a large portion of the hydrogen chloride gave after 0.6 hour a clear yellow solution. After four hours, an increase in pressure had occurred and the solution had become cloudy with precipitated aluminum chloride (Table I).

The reactants were returned to the reaction tube and the temperature raised to −45°. Immediately a brown lower layer formed. Soon thereafter all the white solid had dissolved and the upper layer was bright yellow in color. The lower layer was very small. The equilibrium pressures were then determined in the usual manner as the amount of hydrogen chloride was varied. Results are summarized in Table II.

TABLE II

EQUILIBRIUM PRESSURES OF HYDROGEN CHLORIDE IN PRESENCE OF EXCESS TOLUENE AT −45.4° WITH AND WITHOUT ALUMINUM CHLORIDE

Hydrogen chloride, mmoles	Press., mm.	Temp., °C.	Press., mm. (cor. to −45.4°)
Without aluminum chloride			
1.177	12.9	−45.9	13.2
1.331	97.7	−45.9	94.5
2.368	174.6	−45.9	176
3.385	253.5	−45.4	253.5
2.335	173.6	−45.4	173.6
With aluminum chloride (0.36 mmole $AlCl_3$)			
1.395	87	−45.4	87
2.339	159	−45.4	159
3.296	232	−45.4	232
0.177	0.0	−45.4	0.0

The decrease in pressure of hydrogen chloride (Fig. 2) corresponds to a ratio of $AlCl_3$ to HCl in the complex of 1.8:1. In a check experiment a ratio of 2.1:1 was obtained. Rapid removal of the hydrogen chloride at −45° left 0.177 mmole of hydrogen chloride united with the 0.36 mmole of aluminum chloride, a ratio of 2.0:1 (Table II). Additional hydrogen chloride is given off only very slowly at this temperature, more rapidly at higher temperatures.

A total of 8.176 mmoles of hydrogen chloride was recovered; 8.156 mmoles had been used, so the recovery was 100.2%. The toluene recovered was tensiometrically homogeneous and exhibited a vapor pressure of 6.8 mm. at 0°, identical with that of the original sample. The recovery was 99.8%. The aluminum chloride remaining in the tube had a slight yellow tinge; analysis by the method of Snyder[19] gave 0.365 mmole of aluminum.

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[19] L. J. Snyder, *Ind. Eng. Chem., Anal. Ed.*, **17**, 37 (1945).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Molecular Dimensions of Natural Rubber and Gutta Percha[1]

BY H. L. WAGNER AND P. J. FLORY

The unperturbed end-to-end dimensions $(\overline{r_0^2})^{1/2}$ of *cis*-polyisoprene (natural rubber) and *trans*-polyisoprene (gutta percha) have been determined from intrinsic viscosities measured at the limiting critical miscibility temperature (Θ) for $M = \infty$ in methyl *n*-propyl ketone and in *n*-propyl acetate, respectively. Several fractions of each polymer were used; molecular weights were determined osmotically. $K = [\eta]_\Theta/M^{1/2}$ is independent of M, in accordance with previous observations on a number of other polymer systems. The value of $(\overline{r_0^2}/M)^{1/2}$ calculated from K for gutta percha is about 25% greater than that for rubber. This is in approximate agreement with calculations based on the chain structure assuming free rotation. However, both polymers are appreciably more extended than would be predicted for free rotation, even in the absence of perturbations arising from polymer–solvent interaction.

Introduction

A method for the determination of characteristic dimensions of polymer molecules from appropriate viscosity measurements has been established in previous papers.[2–5] The following relationships are employed

$$[\eta] = KM^{1/2}\alpha^3 \qquad (1)$$

$$\alpha^5 - \alpha^3 = 2\psi_1 C_M (1 - \Theta/T)M^{1/2} \qquad (2)$$

$$K = \Phi(\overline{r_0^2}/M)^{3/}$$

where $(\overline{r_0^2})^{1/2}$ is the root-mean-square distance from beginning to end of the chain *in the absence of perturbations due to interactions between remotely connected segments*, and α is the factor by which the actual root-mean-square distance $(\overline{r^2})^{1/2}$ exceeds this unperturbed distance in a particular solvent at a given temperature; K is a parameter which is characteristic of the polymer but independent of the solvent; and Φ is a hydrodynamic constant which

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[1] This investigation was carried out at Cornell University in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.

(2) P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949).

(3) P. J. Flory and T. G. Fox, Jr., THIS JOURNAL, **73**, 1904 (1951).

(4) T. G. Fox, Jr., and P. J. Flory, *ibid.*, **73**, 1909 (1951).

(5) T. G. Fox, Jr., and P. J. Flory, *ibid.*, **73**, 1915 (1951).

should be the same for all polymers; M is the molecular weight; Θ is the critical miscibility temperature for a polymer of infinite molecular weight in the given solvent; C_M is a constant calculable from theory and ψ_1 is a dimensionless parameter representing the ratio of the entropy of dilution of polymer segments to Rv_2^2 in dilute solution, where v_2 is the volume fraction of polymer.

As a first step toward application of the above equations, the critical consolute temperature (T_c), below which two stable *liquid* phases may coexist, is determined by locating the maximum in the plot of precipitation temperature against composition. According to theory[4,6]

$$T_c \cong \Theta(1 - b/M^{1/2}) \qquad (4)$$

where b is a constant. Hence Θ, for polymer fractions of a given series in a particular solvent, may be obtained from the intercept of T_c plotted against $1/M^{1/2}$. Since according to equation (2) $\alpha = 1$ at $T = \Theta$, it follows from equation (1) that K may be calculated from the intrinsic viscosity measured at the temperature Θ, provided M is known. Making use of present estimates of the constant Φ,[4] the ratio of the square of the unperturbed end-to-end distance to the molecular weight may be found from equation (3).

The general validity and usefulness of the procedure outlined above has been amply demonstrated in the case of polyisobutylene, the intrinsic viscosities of which have been determined over wide ranges of temperature and molecular weight.[4] In the present paper this procedure is applied to the determination of the unperturbed dimensions of two naturally occurring isomeric hydrocarbon polymers, gutta percha and natural rubber. Calculations of Wall[7] based on the assumption of free rotation about all single bonds of these 1,4-polyisoprene chains show that the *trans*-isomer (gutta percha) should be considerably more extended than the *cis*-isomer (natural rubber).

Both natural rubber and gutta percha are sensitive to oxidative degradation. Special precautions were taken, therefore, to avoid elevated temperatures and to exclude oxygen and sunlight. The fact that gutta percha is crystalline at ordinary temperatures poses a further difficulty: it may crystallize from solution rather than precipitate in amorphous form, thus preventing determination of the consolute temperature for separation into two liquid phases. Hence a solvent was required in which Θ is sufficiently high to permit realization of the liquid–liquid phase separation unobstructed by crystallization from solution without, however, being so high as to risk excessive degradation during viscosity measurements at this temperature. *n*-Propyl acetate, for which $\Theta = 333°$K., proved satisfactory. Inasmuch as the melting point of natural rubber is substantially lower, intrinsic viscosities could be measured in methyl *n*-propyl ketone at the somewhat lower Θ temperature, 287.5°K., for this polymer–solvent pair.

Experimental

Polymers and Fractionation.—Two samples of gutta percha[8] were fractionated. The first (I) was separated from resinous impurities by crystallization from a benzene–acetone mixture. The second (II) designated as "precipitated balata" had been purified by the supplier. No evidence for the presence of any *cis*-polyisoprene was found from measurements of the infrared absorption of Sample II.[9] Its carbon and hydrogen analysis conformed to the empirical formula C_5H_8.

The fractionation of the gutta percha was carried out at 30° in the dark under carbon dioxide by the addition of methanol to a 1% solution of the polymer in benzene containing 0.05% phenyl-β-naphthylamine. The fractionation was conducted as previously described for other polymers.[10] The intrinsic viscosity in benzene at 30° and the amount of each fraction expressed as the per cent. of the whole polymer are given in Table I.

"Pale crepe" natural rubber was extracted with acetone in a Soxhlet extractor for two days to remove protein and resins. It was then fractionated in the dark at 5° under an atmosphere of carbon dioxide by precipitation from a 1% toluene solution containing phenyl-β-naphthylamine as above, using methanol as the precipitant. The first fraction, which probably contained most of the impurities not removed by the extraction, was discarded; data pertaining to those of the fractions used here are given in Table I.

Table I

Fraction	% of whole polymer	$[\eta]$ benzene, 30°	$\overline{M}_n$	T_c, °C.	Γ_2 in benzene at 15° (g./100 ml.)$^{-1}$
			Natural Rubber		
NR IIAf$_2$	20.5	1.96	280,000 (±15,000)	7.6	1.29
NR IIBf$_1$	6.2	1.34	164,000 (±10,000)	6.5	0.93
NR IIBf$_2$	4.0	1.06	119,000 (± 6,000)	5.1	.77
NR IIBf$_3$	3.0	0.750	74,500 (± 1,600)	1.3	.49
			Gutta Percha		
GP IIf$_1$	7.2	2.88	210,000 (±11,000)	48.0	1.48
GP IIf$_2$	19	2.43	194,000 (±13,000)	45.8	1.48
GP I f$_1$	9.7	1.86	103,000 (± 7,000)	42.0	1.00

Solvents.—All solvents used in osmotic, precipitation and viscosity measurements were carefully dried and distilled before use. A small amount of 2,5-di-*t*-butylhydroquinone (0.1%) was added to each solvent in order to minimize degradation.

Determination of Molecular Weights.—Number average molecular weights were determined from osmotic pressure measurements in benzene solution at 15° using osmometers designed by S. G. Weissberg and collaborators at the National Bureau of Standards.[11] Each of these osmometers, which resemble that described by Sands and Johnson,[12] consists of a metal cell containing a conical cavity 2–3 ml. in volume which is occupied by the solution. The membrane is placed horizontally over the base of the cone. A "Trubore" 0.10-cm. capillary about 15 cm. in length is attached through a taper joint at the apex of the conical cell. The entire osmometer assembly is immersed in solvent contained in a large flat-bottom test-tube. A reference capillary of the same diameter is immersed in the solvent. Owing to the compact design of these osmometers, it was possible to mount six of them on a revolving stand which was placed in a water thermostat maintained at 15.000 ±

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[6] P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

[7] F. T. Wall, *ibid.*, **11**, 67 (1943).

[8] Supplied by Hermann Weber and Co., New York, N. Y.

[9] We are indebted to Drs. T. W. Dewitt and A. Sacher of the Mellon Institute for these measurements.

[10] P. J. Flory, This Journal, **65**, 375 (1943).

[11] The authors are grateful to Dr. Weissberg for providing a drawing of the osmometer.

[12] George D. Sands and B. L. Johnson, *Anal. Chem.*, **19**, 261 (1947).

0.005°. They could be rotated successively into position for measurements of the liquid levels with a cathetometer reading to ±0.005 cm. The low temperature was chosen to minimize degradation.

Membranes of denitrated collodion were prepared by the method of Montonna and Jilk,[13] except that after the denitration they were washed with water instead of carbon disulfide. In order to obtain somewhat thinner membranes the amount of collodion was reduced; 30 ml. of a mixture of two parts of Merck C.P. collodion (5%) and one part of ethyl ether were used with a ring 6.25 inches in diameter. Those membranes giving permeation rates (d $\log_{10} \Delta h/dt$, in hours^{-1}) of 0.1 to 0.3 at 15° for benzene were selected for use. They lasted indefinitely unless accidentally punctured. The equilibrium difference in level with the solvent on both sides of the membrane never exceeded 0.02 cm. after waiting for at least 24 hours and generally was less than 0.01 cm. No "blank" correction was required therefore.

To prepare a solution of a given concentration a weighed sample of the polymer in a 25-ml. volumetric flask was diluted at 15.0° with benzene containing 0.1% 2,5-di-*t*-butylhydroquinone as antioxidant. Most determinations were performed in duplicate.

After each run the cell was filled with solvent and allowed to stand overnight before rinsing and refilling with the solution to be used in the next experiment. Concentrations were so chosen as to yield Δh values no smaller than about 0.3 cm., the lowest value for which reproducible results were generally obtainable, and no greater than that value for which $(\pi/c)/(\pi/c)_0$ would exceed 2 or 3, the upper limit of usefulness of the extrapolation procedure employed[14] (*cf. seq.*).

After the osmometer was placed in the bath and temperature equilibrium was attained the difference in levels was adjusted to the expected equilibrium pressure. In cases where the initial rate indicated this estimate to be incorrect, another adjustment was made. Equilibrium was generally attained within about 24 hours, no significant changes occurring after this time.

Precipitation Temperatures.—A solution of polymer was placed in a test-tube the top of which was connected to a small bulb half filled with Drierite in order to prevent absorption of moisture.[15] Precipitation was detected by the blurring of an object observed through the solution as the temperature was varied slowly, as described previously.[4] Mechanical stirring was unnecessary.

Viscosity Determinations.—Viscosity measurements were carried out in the manner previously described[4] except that 2,5-di-*t*-butylhydroquinone was used as the antioxidant. The results were extrapolated to infinite dilution but not to zero rate of shear since the correction is not likely to be greater than 1% for the molecular weights used here. Intrinsic viscosities are expressed in (g./100 ml.)$^{-1}$.

Results

Precipitation Temperatures.—The precipitation temperatures (T_p) of a given fraction of rubber in methyl *n*-propyl ketone were determined at several concentrations from 0.5 to 5 or 6% of polymer. An example of a plot of T_p *versus* c is shown in Fig. 1 for one of the fractions. The consolute temperature, or the maximum temperature for the coexistence of two liquid phases, is the maximum in this curve; these are given for each fraction in Table I. When this consolute temperature is plotted against $M^{-1/2}$ in accordance with equation (4) linear extrapolation leads to 287.5 ± 2 °K. for Θ (see Fig. 2).

In the case of gutta percha special precautions are necessary to distinguish between crystallization of the polymer ("crystalline precipitation") and the separation into two liquid phases ("amorphous precipitation"). The required critical temperature Θ is that for liquid–liquid equilibrium. If crystalline precipitation is involved, the observed separation temperature increases monotonically with concentration, whereas with amorphous precipitation a maximum (T_c) is observed at a low concentration (see Fig. 1). Consequently, if T_p is observed to decrease with increasing concentrations at higher concentrations, amorphous precipitation is indicated. In the case of a crystalline polymer such as gutta percha, crystallization always takes place at a sufficiently high concentration but whether amorphous precipitation occurs at lower concentrations in a given solvent depends on the temperature, the molar volume of the solvent, the melting temperature of the polymer, the heat of fusion of the polymer and the thermodynamics of the interaction between the polymer and the given solvent.[16]

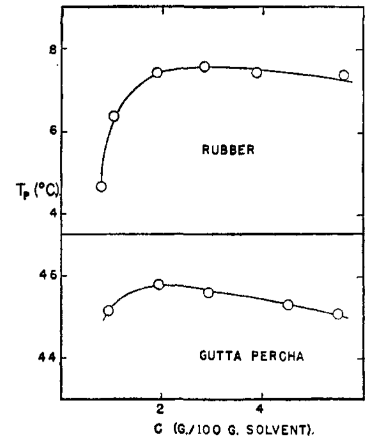

Fig. 1.—Dependence of the precipitation temperature on concentration of polymer: top, natural rubber (fraction IIAf$_2$) in methyl *n*-propyl ketone; bottom, gutta percha (fraction IIf$_2$) in *n*-propyl acetate.

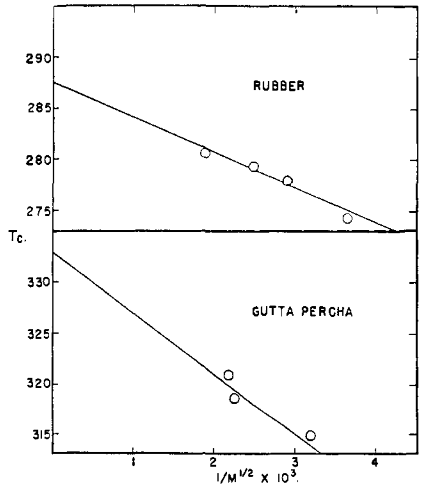

Fig. 2.—The dependence of the critical precipitation temperature on the reciprocal of the square root of the molecular weight: top, natural rubber in methyl *n*-propyl ketone (Θ = 287.5°K.); bottom, gutta percha in *n*-propyl acetate (Θ = 333°K.).

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[13] R. E. Montonna and L. T. Jilk, *J. Phys. Chem.*, **45**, 1374 (1941).

[14] T. G. Fox, Jr., P. J. Flory and A. M. Bueche, THIS JOURNAL, **73**, 285 (1951).

[15] We are indebted to Mr. Allan R. Shultz for devising this procedure.

[16] P. J. Flory, L. Mandelkern and H. K. Hall, THIS JOURNAL, **73**, 2532 (1951).

Fortunately, a suitable solvent, *n*-propyl acetate, was found for which Θ (333°K. or 60°C.) lies in the optimum range from the standpoint of compromising the complications arising from the possible crystallization of the gutta percha on the one hand with the hazard of degradation at higher temperatures on the other. The three highest fractions definitely exhibited amorphous precipitation. Owing to the decrease in T_c with decrease in M, those of lower molecular weight separated in crystalline form; hence these fractions were not employed in establishing the value of Θ. Because of the limited range of molecular weight that is available, it is only possible to assume that T_c is linear in $1/M^{1/2}$ and to draw the best straight line through the points as in Fig. 2. The resulting uncertainty in Θ is ± 5°, which is of no consequence for the purposes of this investigation.

Molecular Weights.—The extrapolation method described by Fox, Flory and Bueche[14] was applied to the osmotic pressure data. Experimental values of log (π/c) (the points of Fig. 3) were plotted against log c and the data thus expressed were fitted to the theoretical graph of

$$\log [(\pi/c)/(\pi/c)_0] = \log (1 + \Gamma_2 c + 5/8\, \Gamma_2{}^2 c^2) \quad (5)$$

against log $(\Gamma_2 c)$ (the lines of Fig. 3). Log $(\pi/c)_0$ was obtained by comparison of the ordinate scales of the experimental and theoretical plots. Log Γ_2 was found by a similar comparison of abscissas. The molecular weights M calculated from $(\pi/c)_0 = RT/M$ are listed in Table I. The average uncertainty is about ±6%. Values of Γ_2 are also given in Table I.

The osmotic data presented in Fig. 3 are shown again in Fig. 4 according to the conventional π/c vs. c plot. The lines drawn through the points are those calculated from equation (5) using the values of the parameters, $(\pi/c)_0 = RT/M$ and Γ_2 (see Table I), established in Fig. 3. The data are not sufficiently accurate to be presented as further evidence in support of equation (5). However, the essential validity of extrapolation according to this relation is well founded in theory[17] and its experimental confirmation has been discussed previously.[14] The osmotic data are adequate for ascertaining molecular weights to the required accuracy. Linear extrapolation of π/c with c would, however, lead to errors which are significant. For example, the molecular weight so obtained for rubber fraction IIAf$_2$ would be about 350,000, compared with 280,000 according to the above method.[18]

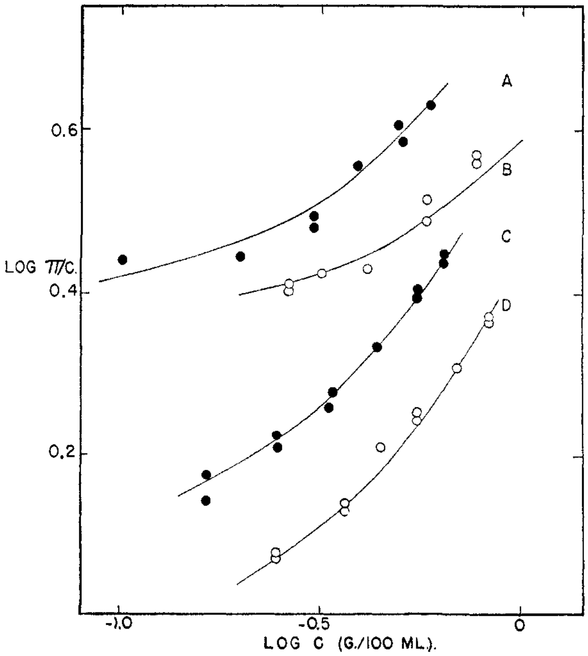

Fig. 3.—Examples of osmotic pressure results: points represent experimental data for benzene solutions at 15°; each line represents the "best fit" of the curve calculated from equation (5); A, gutta percha fraction If$_1$; B, natural rubber fraction IIBf$_3$; C, gutta percha fraction IIf$_3$; D, natural rubber fraction IIAf$_2$.

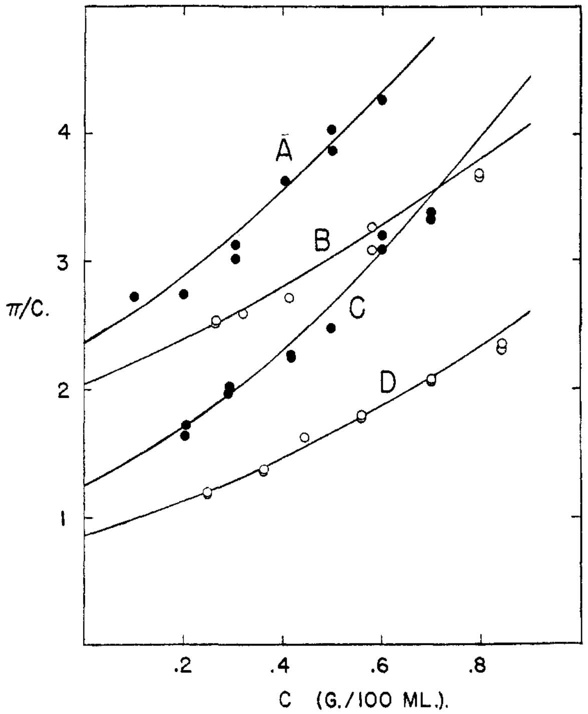

Fig. 4.—Osmotic data shown in Fig. 3 re-plotted as π/c vs. c. Curve designations are the same as given in legend for Fig. 3.

Intrinsic Viscosities.—The intrinsic viscosity of each fraction of rubber and gutta percha in benzene at 30° is reported in Table I. More extensive intrinsic viscosity measurements on several of the fractions at various temperatures in poor solvents are reported in Table II. The intrinsic viscosity of rubber fraction IIBf$_3$ was measured also in toluene, a good solvent, from 0 to 60°. Over this range it is independent of temperature within experimental error. Viscosities of gutta percha

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(17) P. J. Flory, *J. Chem. Phys.*, **17**, 1347 (1949); P. J. Flory and W. R. Krigbaum, *ibid.*, **18**, 1086 (1950).

(18) Our molecular weight values for natural rubber appear to be somewhat greater than those calculated from intrinsic viscosities in toluene at 25° using the empirical relation $[\eta] = 5.02 \times 10^{-4} M^{0.667}$, of Carter, Scott and Magat, This Journal, **68**, 1480 (1946). Measurements on our fraction in toluene at 25° give $[\eta] = 2.0 \times 10^{-4} M^{0.73}$. The two relationships are coincident in the vicinity of $M = 5 \times 10^5$; the latter gives molecular weights about 15% higher at $M = 10^6$.

could not be measured in *n*-propyl acetate below about 55° because of precipitation; measurements were not extended above 67° on account of the hazard of degradation. Intrinsic viscosities at the estimated Θ temperature, given in parentheses in Table II, were obtained by interpolation.

TABLE II

INTRINSIC VISCOSITY OF NATURAL RUBBER IN METHYL *n*-PROPYL KETONE

Fraction →	IIAf$_2$		IIBf$_1$		IIBf$_2$	
Temp., °C.	$[\eta]$	α	$[\eta]$	α	$[\eta]$	α
7	0.60	0.96	0.414	0.96	0.305	0.98
12	.64	0.98	.442	.98	.317	.99
(14.5) (Θ)	(.67)		(.462)		(.322)	
20	.72	1.03	.498	1.03	.328	1.01
40	.84	1.08	.542	1.06	.350	1.03

INTRINSIC VISCOSITY OF NATURAL RUBBER IN TOLUENE (Fraction IIBf$_2$)

Temp., °C.	$[\eta]$
0	0.80
30	.80
60	.77

INTRINSIC VISCOSITY OF GUTTA PERCHA IN *n*-PROPYL ACETATE

Fraction →	IIf$_2$	If$_1$
Temp., °C.	$[\eta]$	$[\eta]$
55	1.02	0.73
(60) (Θ)	(1.06)	(.72)
61.7	1.07	.72
67	1.08	.72

Discussion

Polymer Dimensions.—The value of K computed according to equation (1) from the molecular weight of each fraction and from its intrinsic viscosity at $T = \Theta$ (where $\alpha = 1$; see equation (2)) is given in Table III. Since the temperature coefficient of the intrinsic viscosity of natural rubber in *n*-propyl ketone does not exceed 1% even for the fraction of highest molecular weight (see Table II), the error in Θ of ±2° is reflected as an error of not more than 2% in K. Similarly, in the case of gutta percha, for which the temperature coefficient is of the order of 0.5% per degree, the uncertainty of ±5° in Θ introduces an uncertainty of 3% in K. For both rubber and gutta percha the values obtained for K are independent of the molecular weight of the fraction within experimental error.

TABLE III

Fraction	Mn	$K \times 10^3$	$(\overline{r_0^2}/M)^{1/2} \times 10^{11}$ Calcd. from K	$(\overline{r_0^2}/M)^{1/2} \times 10^{11}$ Calcd. free rot.
	Natural Rubber ($\Theta = 287.5$ °K.)			
IIAf$_1$	280,000	1.26		
IIBf$_1$	164,000	1.14		
IIBf$_2$	74,500	1.18		
		(av. 1.19)	830	485
	Gutta Percha ($\Theta = 333$ °K.)			
IIf$_2$	194,000	2.40		
If$_1$	103,000	2.24		
		(av. 2.32	1030	703

The values of $(\overline{r_0^2}/M)^{1/2}$ given in the next to last column of the table were calculated from the average K's, assuming for Φ of equation (3) the tentative value of 2.1×10^{21},[4] The unperturbed root-mean-square end-to-end distance for gutta percha appears to be 1.24 times that for natural rubber of the same molecular weight.

Wall[7] has derived expressions for the ratio of the mean-square unperturbed end-to-end length $(\overline{r_0^2})$ to the degree of polymerization for *cis*- and *trans*-polyisoprene molecules, assuming free rotation about all single bonds of the chains. The "free rotation" values of $(\overline{r_0^2}/M)^{1/2}$ calculated from Wall's formulas are listed in the last column of Table III. Hindrances to free rotation should be expected to alter these calculated dimensions, perhaps to different degrees in the respective structures. Indeed, the actual end-to-end dimensions of both rubber and gutta percha are appreciably greater than the calculated free rotation dimensions; the ratio of the experimental to the theoretical free rotation end-to-end distance for rubber is 1.7, while that for gutta percha is 1.5. The larger value for the former may reflect incidence of greater local steric interactions in the more compact *cis* chain.

The K's for the two isomeric polyisoprenes have been determined in each case at one temperature only (for reasons dictated by the experimental difficulties set forth above) and the respective temperatures employed for the two polymers are about 45° apart. In order to ascertain the extent to which the conclusions drawn above may depend on the particular temperatures chosen, it is important to gain some idea of the temperature coefficient of K, and hence of $(\overline{r_0^2}/M)^{1/2}$. An estimate of $\mathrm{d}K/\mathrm{d}T$ may be obtained from the temperature coefficient of the intrinsic viscosity measured in a nearly athermal solvent ($\Theta \cong 0$). Thus, combining equations (1) and (2)

$$K^{2/3} = \frac{[\eta]^{5/3}\,M^{-1/3}}{[\eta] + 2KC_{\mathrm{M}}\,\psi_1 M(1 - \Theta/T)} \tag{6}$$

From the definition of C_{M} given elsewhere[3] it is seen that the product KC_{M} is very nearly independent of temperature

$$KC_{\mathrm{M}} = (27/2^{5/2}\,\pi^{3/2})\,(\bar{v}^2/N\mathrm{v}_1)\Phi \tag{7}$$

where $\bar{v}$ is the specific volume of the polymer, v_1 is the molar volume of the solvent, and N is Avogadro's number. Equation (6) may then be differentiated with respect to T, treating KC_{M} as a constant

$$\frac{\mathrm{d}K}{\mathrm{d}T} = (3/2)K^{1/3}M^{-2/3}\Big[[\eta] + 2C_{\mathrm{M}}K\psi_1 M(1 - \Theta/T)\Big]^{-2} \times \left\{\left[\frac{\mathrm{d}[\eta]}{\mathrm{d}T}\,M^{1/3}\right]\Big[2/3[\eta]^{5/3} + (10/3)\,C_{\mathrm{M}}KM\psi_1(1 - \Theta/T)[\eta]^{2/3}\Big] - [\eta]^{5/3}\,M^{4/3}\,2C_{\mathrm{M}}K\psi_1\,\Theta/T^2\right\} \tag{8}$$

According to the results of Meyer, Wolff and Boissonnas[19] the heat of dilution of rubber in toluene is very small; *i.e.*, for this system $\Theta \cong 0$. The results included in Table II show that $\mathrm{d}[\eta]/\mathrm{d}T$ for rubber in toluene is zero within experimental error, and certainly does not exceed 5×10^{-4} in magnitude. $2C_{\mathrm{M}}\psi_1$ may be calculated according

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(19) K. H. Meyer, E. Wolff and Ch. G. Boissonnas, *Helv. Chim. Acta*, **23**, 430 (1940).

to equation (2) through the use of α's established from the intrinsic viscosity in toluene, Θ being assumed equal to zero. Substituting the resulting quantities along with $K_{14.5°} = 1.2 \times 10^{-3}$ into equation (6), the maximum change in K would amount to 12% in 100°; a similar result is obtained if Θ is taken to be 100°K. and $d[\eta]/dT = 0$. Thus, $(\overline{r_0^2}/M)^{1/2}$ for rubber must be approximately independent of temperature, from which it follows that conversion of the K and $(\overline{r_0^2}/M)^{1/2}$ values for rubber to 60°, the temperature at which determinations were carried out on gutta percha, would not affect the conclusions reached above.

Thermodynamic Parameters.—By computing $(\alpha^5 - \alpha^3)/M^{1/}$ from the α's listed in Table II for rubber in methyl n-propyl ketone and plotting this function against $1/T$ (see equation (2)), it is found that $2C_M\psi_1 = 0.0049$. Employing equation (7), $C_M = 0.0288$, giving $\psi_1 = 0.085$. This value for ψ_1 is comparable to those found for polyisobutylene; since the temperature range is quite limited, the uncertainty probably is of the order of ± 0.05, however. The gutta percha data are inadequate for such calculations.

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Acetic Acid—Ammonium Acetate Reactions. An Improved Chichibabin Pyridine Synthesis[1]

BY MARVIN WEISS

Acetic acid containing varying concentrations of ammonium acetate is examined as a medium for the synthesis of nitrogen heterocycles. These conditions have previously been found useful in the formation of substituted imidazoles, pyrazines, pyrroles, oxazoles and piperidones. The method has now been extended to include arylated pyridines, acetic acid being replaced by acetamide in the more sluggish reactions. A mechanism is proposed for pyridine ring formation in the Chichibabin synthesis.

In a series of papers by Davidson, Weiss and Jelling,[2a,b,c] the rather complex reactions of ammonia on benzil and benzoin were elucidated. The unusual approach to this problem was in the use of ammonium acetate in acetic acid as a source of ammonia.[3a,b,4] It was found that under simple reflux in this medium, excellent yields of single products were isolated, with minor amounts of other products. This procedure, which led to convenient methods of synthesizing imidazoles (Table I) (A), pyrazines (B), oxazoles (C) and pyrroles (D), stood in sharp contrast to that of the early investigators, who used alcoholic ammonia or fused ammonium salts in sealed tubes. Noller and Baliah[5] later applied this reaction medium in a modification of the Petrenko–Kritschenko piperidone synthesis (E). The success of these conditions probably depends upon the fact that such base-catalyzed condensations are sometimes facilitated by the inclusion of acids.[6]

TABLE I

APPLICATIONS OF THE ACETIC ACID–AMMONIUM ACETATE METHOD TO THE SYNTHESIS OF N-HETEROCYCLES

	Reactants	Ring type
A[2a]	Benzil + aldehydes	Imidazoles
B[2b]	Benzoins	Pyrazines
C[2b]	Benzoin esters	Oxazoles
D[2c]	Benzoin + $RCOCH_2R'$	Pyrroles
E[5]	$RNH_2 + R'CHO + R^2CH_2COCHR^3R^4$	Piperidones
F	$RCHO + C_6H_5COCH_2R'$	Pyridines

The most useful aspect of this method is that competitive reactions may be almost entirely eliminated by varying the ammonium acetate concentration. The more reactive donors require less ammonium acetate. However, the apparent sluggishness of methyl ketones as donors in the Chichibabin synthesis (F) allows aliphatic aldehydes to self-condense.[7]

The history of the Chichibabin pyridine synthesis is similar to the ammonia reactions mentioned previously. Frank and Seven[8] revealed in a recent careful study that there were but few instances of yields higher than 20%. Sealed tubes, high temperatures and vapor reactions over heated catalysts were necessary. While Frank and Seven modified the synthesis by employing aqueous ammonia and catalytic amounts of ammonium acetate and so produced favorable yields of single products, they still required the use of a steel autoclave at temperatures of 250° with pressures up to 1450 p.s.i.

The present investigation deals with the reaction of aromatic aldehydes with aryl alkyl ketones containing a methylene group, the reaction being conducted in glacial acetic acid in the presence of ammonium acetate. Under these conditions it was found that the aldehyde appears as a substituent in

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[1] Presented at the Meeting-in-Miniature, Metropolitan Long Island Sub-Section, March, 1951.

[2] (a) Davidson, Weiss and Jelling, *J. Org. Chem.*, **2**, 319 (1937); (b) *ibid.*, **2**, 328 (1937); (c) Davidson, *ibid.*, **3**, 361 (1938).

[3] (a) Davidson, THIS JOURNAL, **58**, 1821 (1936); (b) Davidson and Epstein, *J. Org. Chem.*, **1**, 305 (1936).

[4] In an early isolated case Angelico and Calvello, *Gazz. chim. ital.*, **31**, II, 7 (1901), used this reaction medium to produce 2,3,5-triphenylpyrrole from ω-desylacetophenone.

[5] Noller and Baliah, THIS JOURNAL, **70**, 3853 (1948).

[6] E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 180.

[7] Frank and Riener, THIS JOURNAL, **72**, 4182 (1950).

[8] Frank and Seven, *ibid.*, **71**, 2689 (1949).