smaller than in gelatin gels and far greater than in synthetic polymer solutions, and the rigidities are smaller than in either. The elastic mechanisms are probably quite different from those of either of the more familiar systems.

Kirkwood and Auer[19] showed that a dilute solution of rigid rod-like molecules should exhibit a dynamic rigidity with Maxwellian dispersion; the limiting high-frequency value for the intrinsic rigidity, G'/c, should be $3RT/5M$ in our units, where M is the molecular weight. This theory can hardly be strictly applicable to SDNA in our concentration range, since it is designed for isolated molecules; in the absence of intermolecular interference, SDNA molecules should orient in water with a relaxation time[33] of about 0.01 sec. instead of 1 sec., and this situation is reached[7] only below 0.00002 g./ml. Nevertheless, the SDNA molecule is apparently rigid and extended,[33–35] and it is of interest therefore to calculate the intrinsic rigidity from the above formula. Taking $M = 8 \times 10^6$, G'/c is found to be 1850 (dynes/cm.^{2}) (g./ml.)$^{-1}$. This value is actually of the correct order of magnitude, and is plotted in Fig. 4 with a dotted line to show how it might be approached at infinite dilution. It is tentatively concluded that not only the viscosities but also the rigidities of SDNA solutions involve primarily the orientations of rigid elongated particles which are crowded together with marked steric hindrance, but form no interconnecting structure through bonds or localized attractive forces.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, TEXAS DIVISION, MONSANTO CHEMICAL COMPANY]

Physical Properties of *o*-, *m*- and *p*-Methylstyrene

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High purity *o*-, *m*- and *p*-methylstyrene were prepared from purified samples of the corresponding bromotoluenes. The vapor pressure, index of refraction, density and freezing point were measured for each isomer. Other derived physical properties are reported also.

In connection with their possible uses as monomers, certain physical properties of high purity samples of the methylstyrenes were measured. The methylstyrenes were prepared from the corresponding bromotoluenes by well known methods.[1]

To assure high purity in the final products, the bromotoluenes (starting materials from Eastman Kodak Co.) were each fractionated in a 100-plate column operating at 50:1 reflux ratio. The middle 80% was recovered as product for the preparation of the appropriate tolylmagnesium bromide. Each of the bromotoluenes was assayed for purity before and after fractionation by freezing point methods and equipment described by Taylor and Rossini.[2]

Table I shows the mole per cent. impurity of the bromotoluene samples before and after fractionation, together with our best values of the freezing point for zero impurity (T_{f0},°C.) each of which is the mean of three independent freezing experiments. The impurity concentrations were calculated assuming the cryoscopic constant of all the bromotoluenes to be 0.0242 mole fraction/°C.

All lots of purified methylstyrenes were also assayed by cryoscopic techniques and only those samples assaying 99.4 mole % or better, were used in any measurements reported here. All measured physical properties are given in Table II together with conservative estimates of uncertainties wherever possible. Standard deviations of the vapor pressure measurements are those calculated from the deviations of the measured pressures from the pressures calculated from the Antoine equation fit.

TABLE I

IMPURITY CONCENTRATIONS IN BROMOTOLUENES

	Mole per cent. impurity		
	Original	Purified	T_{f_0}, °C.
o-Bromotoluene	0.33	0.02	-26.81 ± 0.04[a,b]
m-Bromotoluene	1.03	.38	$-38.14 \pm .04$
p-Bromotoluene	1.04	.07	$+26.58 \pm .04$

[a] J. Timmermans ("Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950, pp. 298–299) gives the freezing point of *o*-bromotoluene as −28.1° and *p*-bromotoluene as +26.7°. [b] All uncertainties of physical data reported in this paper will be in standard deviation units (1 sigma limits, *i.e.*, $\pm\sigma$).

Experimental

Vapor Pressure Measurements.—The vapor pressures were measured by a static method. All measured point-pairs of temperature and pressure were fitted to the three-constant Antoine equation by the method of least squares described by Rossini, *et al.*[3]

The apparatus used in the vapor pressure measurements consisted of a differential manometer made from two 6 in. long tubes 16 mm. inside diameter. To the bottom bend

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[1] Y. Hirschberg, THIS JOURNAL, **71**, 3241 (1949).

[2] W. J. Taylor and F. D. Rossini, *J. Research Natl. Bur. Standards*, **32**, 197 (1944).

[3] C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *ibid.*, **35**, 219 (1945).

TABLE II

SUMMARY OF MEASURED PHYSICAL PROPERTIES OF THE METHYLSTYRENES

		Ortho-	Meta-	Para-
Vapor pressure[a] constants in Antoine eq.[b] for temp. range 20-120°	A	7.15272	6.95079	7.04830
	B	1628.405	1520.412	1594.747
	C	211.386	201.967	209.889
σ, p.mm.		±0.06	±0.12	±0.10
n^{20}_D ±0.00005		1.54374	1.54114	1.54202[c]
dn_D/dt (25°)		−0.00048	−0.00052	−0.00051
Density, g./ml. ±0.0002	0°	0.9284	0.9283	0.9383
	25°	.9077	.9076	.9173[d]
	35°	.8992	.8992	.9088
Freezing point for zero impurity, °C.		−68.57 ± 0.04	−86.34 ± 0.14	−34.15 ± 0.11[e]

[a] F. R. Buck, *et al.*, *J. Chem. Soc.*, 2377 (1949), use the equation $\log_{10}P_{mm} = (a/T) + b \log_{10} T + c$ for the range 80–120° and find for *m*-methylstyrene, $a = -3563$, $b = -7.553$ and $c = 30.90$ and for *p*-methylstyrene, $a = -3476$. $b = -6.923$ and $c = 29.03$. [b] The Antoine equation is written as $\log_{10}P_{mm} = A - (B/(C + t))$. [c] Buck, *et al.*, ref. *a*, report n^{20}_D 1.5421. [d] Buck, *et al.*, ref. *a*, d^{24}_4 0.893. [e] Buck, *et al.*, ref. *a*. report −37.8° for 98.5 mole % pure *p*-methylstyrene.

of the manometer was sealed a 2 mm. capillary tube which connected to a mercury reservoir. The top of one manometer arm was sealed to a small bulb into which the sample was frozen by vapor-phase transfer while the other manometer arm was connected to a high-vacuum system and the necessary manipulating stopcocks. In this way, by applying pressure or vacuum to the mercury in the reservoir, the mercury was raised to trap the sample vapors in one arm or lowered to allow outgassing of the sample. The whole assembly was connected to the vacuum system through a ground joint in such a way that it could be raised or lowered into the thermostat bath at will. This assembly allowed manometer readings of the vapor pressure to be made with a cathetometer (readable to 0.05 mm.) in a completely isothermal system. In most cases a 5-ml. sample of the methylstyrene was used although even smaller samples could have been taken with no loss of accuracy.

The temperatures were read from a Bureau of Standards calibrated thermometer readable to 0.01°. After the complete apparatus had come to equilibrium with the thermostat, a pressure reading was taken on the manometer. Prior to reading the pressure, however, the mercury in both manometer legs was slowly raised 2–3 mm. in order that the menisci in both legs should be as much alike as possible. This technique avoided the necessity of making capillary depression corrections. The manometer legs were then lowered to expose the liquid sample to the high vacuum system, enabling the light vapors and gases, evolved since the previous evacuation, to be pumped away. After pumping a few seconds, the mercury was again run into the manometer, and, after thermal equilibrium was again achieved, another pressure reading was taken. This outgassing process was in each case carried out at the highest temperature considered practicable for the compound in question, usually near 100°. Successive outgassings at this temperature were continued until constant vapor pressures were obtained. In many cases 7 pumpings were required. Using these techniques with three independently synthesized samples of each isomer, the measured vapor pressure–temperature points in Table III were obtained.

To increase the "thermal inertia" in the sample bulb, it was half-filled with mercury by deliberately spilling over mercury from the manometer. It was desirable to do this since rapid peak-to-peak temperature oscillations in the oil-bath thermostat were observed to be as large as 0.07°. Thus, by increasing the heat capacity of the sample bulb, the effect of transient temperature changes on the vapor pressure were minimized. Long term stability of the thermostat was ±0.01°.

No inhibitors were used in any vapor pressure measurements and no polymer was found after a series was completed. The observed vapor pressures were corrected for the vapor pressure of mercury at the temperature of the measurement as well as the density of mercury corrected to that at 0°.

Refractive Index.—The refractive indexes were measured by means of a Bausch and Lomb precision refractometer in which thermostated water was circulated through the prism blocks. The temperature of the prisms was maintained constant within ±0.03°. A sodium vapor lamp was used as the light source.

TABLE III

COMPARISONS OF MEASURED WITH SMOOTHED VAPOR PRESSURE DATA FOR THE METHYLSTYRENES

t, °C.	$P_{obsd.}$, mm.	$P_{calcd.}$	$\Delta P_{obsd.-calcd.}$
A. *o*-Methylstyrene (9 points)			
32.01	2.90	2.90	0.00
40.85	4.97	4.97	.00
58.51	13.15	13.16	− .01
58.54	13.24	13.18	− .06
70.20	23.35	23.43	− .07
82.80	41.47	41.44	+ .03
82.83	41.51	41.49	+ .02
100.35	84.83	84.93	− .10
112.35	132.75	132.64	+ .11
σ = ± 0.06 mm.			
B. *m*-Methylstyrene (14 points)			
41.78	5.15	5.17	−0.02
43.22	5.58	5.62	− .04
49.90	8.28	8.21	+ .07
52.12	9.46	9.27	+ .19
55.73	11.24	11.24	.00
57.80	12.55	12.53	+ .02
65.20	18.34	18.19	+ .15
70.95	23.94	23.98	− .04
71.01	24.02	24.05	− .03
71.02	24.02	24.06	− .04
71.10	24.36	24.15	+ .21
77.12	31.76	31.84	− .08
99.33	80.23	80.27	− .04
111.80	127.66	127.39	+ .27
σ = ± 0.12 mm.			
C. *p*-Methylstyrene (14 points)			
31.82	2.82	2.82	0.00
41.76	5.17	5.14	+ .03
41.83	5.20	5.16	+ .04
52.17	9.05	9.18	− .13
53.94	9.98	10.09	− .11
59.58	13.48	13.50	− .02
59.91	13.91	13.72	+ .19
66.62	19.04	19.09	− .05
75.40	28.94	28.73	+ .19
76.19	29.81	29.77	+ .04
80.20	35.39	35.55	− .16
82.44	39.06	39.17	− .11
90.90	55.80	55.77	+ .03
96.93	71.00	70.90	+ .10
σ = ±0.10 mm.			

Density Measurements.—Densities were measured with a Sprengel-type pycnometer having a volume of about 8 ml. All weighings were made on an analytical balance sensitive to 0.1 mg. and were corrected for buoyancy of air in all cases. It is felt that the density measurements reported here are the least satisfactory of the physical properties detailed in Table II.

Freezing Points.—The freezing points of the methylstyrenes, calculated to zero impurity, were obtained necessarily as a consequence of the purity determinations by methods referred to earlier. It should be mentioned here that equilibrium freezing of *m*-methylstyrene is not a simple task. Various workers have observed that meta-substituted aromatics are usually difficult to freeze to crystalline states; they usually freeze to glasses. By carefully inserting a chilled, sandblasted, nichrome wire into the calorimeter containing supercooled *m*-methylstyrene, the compound was made to crystallize after many futile attempts. By allowing the crystalline mass to melt very slowly, a point was ultimately reached when only a small quantity (*ca.* 10 mg.) of crystalline hydrocarbon remained. At this point, the customary freezing experiment was performed in which good equilibrium could usually be obtained. In estimating purities of the samples of methylstyrenes, an estimated cryoscopic constant (by Walden's rule) of 0.0280 mole fraction/°C. was used.

Discussion

Dreisbach and Schrader,[4] using a constant pressure vapor–liquid equilibrium still, similar to one described by Rossini, *et al.*,[3] at the Bureau of Standards, report three pairs of temperature–vapor pressure points for *p*-methylstyrene. Comparing their vapor pressures with vapor pressures calculated from our Antoine equations for all three isomers, it appears (Table IV) that Dreisbach and Schrader actually had the ortho isomer instead of the para. Moreover, their point at 90.98° appears to be in error perhaps due to a typographical error reading 37.16 for 57.16 which still would not be a good check.

TABLE IV

COMPARISON OF VAPOR PRESSURES

Temp., °C.	Vapor pressure in mm. This work *o*-	*m*-	*p*-	Dreisbach and Schrader[4] "*p*-methylstyrene"
90.98	58.50	57.64	55.95	37.16
98.13	77.91	76.63	74.28	77.64
111.16	127.09	124.51	120.49	127.20

Dreisbach and Martin[5] report that *p*-methylstyrene has a freezing point of −70.3°. In Table II we report a freezing point for *o*-methylstyrene of −68.57° which is the only freezing point reasonably close to that of Dreisbach and Martin. Buck, *et al.* (ref. *a*, Table II), list the freezing point of *p*-methylstyrene as −37.8° compared to ours as −34.15°. This again indicates that Dreisbach was working with *o*-methylstyrene and not *p*-methylstyrene as reported by him.

Derived Properties.—From the experimentally determined physical properties in Table II, some derived properties were calculated and are listed in Table V.

TABLE V

DERIVED PHYSICAL PROPERTIES OF *o*-, *m*- AND *p*-METHYLSTYRENE

Property		Ortho-	Meta-	Para-
B.p., °C.	100 mm.	104.64 ± 0.02	105.12 ± 0.03	106.01 ± 0.03
	760 mm.	169.80	171.60	172.78[a]
Heat of vapn., kcal./mole	100 mm.	10.51	10.42	10.38
	760 mm.	9.46	9.27	9.31
Crit. vol., cc./mole		435	435	435
Crit. press., atm.		32.4	32.5	32.6
Crit. temp., °K.		665	668	669
Compressibility factor Z	100 mm.	0.988	0.988	0.988
	760 mm.	0.945	0.945	0.945

[a] Given as 170.5° by Buck, *et al.* (ref. *a*, Table II) and as 171.06° by Dreisbach and Martin.[5]

The boiling points at 100 mm. and 760 mm. pressure were calculated from the Antoine equations. Extrapolation of vapor pressures by the Antoine equation has been discussed by Thomson.[6] It would appear that such an extrapolation is valid up to a reduced temperature of 0.75, above which another Antoine equation should be used. The boiling point calculated at 760 mm. necessitates an extrapolation, in this case, to a reduced temperature of 0.67. This fact lends some assurance to the calculated boiling point at 760 mm. In spite of this, and in the absence of more information, no uncertainty is estimated for these constants.

The heats of vaporization of each isomer at 100 mm. and 760 mm. were calculated from the vapor pressures by an equation given by Rossini.[7] This equation involves the compressibility factor, Z, of the vapor in equilibrium with the liquid. The Z factors were calculated from the Berthelot equation of state wherein the constants are all expressible as functions of the critical properties of the vapor. The critical pressure, temperature and volume were approximated by empirical methods given by Hougen and Watson.[8]

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(7) F. D. Rossini, "Chemical Thermodynamics," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 436.

(8) O. A. Hougen and K. M. Watson, "Chemical Process Principles, Part I, Material and Energy Balances," John Wiley and Sons, Inc., New York, N. Y., 1947, pp. 68–73.