giving low yields of methane plus methyl chloride.[9] These conclusions are entirely consistent with those of Bartlett and Altschul.[10] From the evolution of carbon dioxide from benzoyl peroxide in allyl acetate, they concluded that this gas does not come from a unimolecular decomposition of the benzoate radical but may arise (a) only from some spontaneous decomposition of the peroxide or (b) only from decarboxylation of benzoate radicals during reaction with other molecules. All these considerations suggest that the solvents which by our measurements are found to be "most reactive" toward the radicals from acetyl peroxide are those which are best able to decarboxylate acetoxyl radicals with simultaneous liberation of methane or methyl chloride. (2) Since acetate radicals would be expected to prefer reaction with electron-donor solvents,[11] the low reactivity of carbon tetrachloride is accounted for. (3) Acetate radicals should be more stabilized through resonance than methyl radicals. (4) Although the neophyl radical[12] when prepared by the decomposition of β-phenylisovaleryl peroxide does not rearrange, the neophyl radicals which apparently occur in the reaction of neophyl chloride with either phenylmagnesium bromide or butylmagnesium chloride in the presence of 2–3 mole % cobaltous chloride,[13] or in the peroxide-catalyzed chain decomposition of β-phenylisovaleraldehyde,[14] and which cannot be protected by a carboxyl group, show partial rearrangement. (5) Kharasch and Urry[15] have reported different behaviors of propyl radicals prepared from peroxide decomposition and from Grignard reactions.

Summary

The thermal decomposition of dilute solutions of acetyl peroxide in single and mixed solvents was studied at 60–100°. Investigation of both gaseous and liquid products in a single large run in carbon tetrachloride accounted for 95% of the methyl residues and 87% of the the theoretical carbon dioxide.

The other, small scale, experiments were concerned mostly with the ratio of methane to methyl chloride formed. With carbon tetrachloride as the only solvent, some methane was formed but the proportions of methane and methyl chloride were not reproducible unless a very small proportion of acetic anhydride was added. From the much larger methane:methyl chloride ratios obtained from mixtures of carbon tetrachloride with benzene, toluene, cyclohexane, 1-octene, acetone, methyl acetate, methyl benzoate, or chloroform (which yields mostly methane and little methyl chloride by itself), the relative reactivities of these solvents toward the radicals in decomposing acetyl peroxide were determined. These relative reactivities are so different from those of the same solvents toward the long-chain alkyl and substituted benzyl radicals in polymerizing ethylene and styrene that one of two conclusions is indicated: either (1) methyl radicals behave much differently than other hydrocarbon radicals or else (2), the preferred alternative, the decomposition of acetyl peroxide yields acetate radicals which decarboxylate as they react.

---

[9] The lower over-all yields of gas from "less reactive" solvents may also possibly be due to spontaneous formation of more acetate and fewer methyl radicals in these solvents.

[10] Bartlett and Altschul, THIS JOURNAL, **67**, 812 (1945).

[11] Walling, *ibid.*, **70**, 2561 (1948).

[12] S. Winstein, private communication.

[13] Urry and Kharasch, THIS JOURNAL, **66**, 1438 (1944).

[14] Winstein and Seubold, *ibid.*, **69**, 2916 (1947).

[15] Kharasch and Urry, *J. Org. Chem.*, **13**, 101 (1948).

PASSAIC, N. J. RECEIVED DECEMBER 2, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Magnetic Anisotropy of Dimethyl Terephthalate and Polyethylene Terephthalate

BY P. W. SELWOOD, JOHN A. PARODI[1] AND ANDERSON PACE, JR.[2]

The problem of evaluating molecular orientation in a substantially amorphous polymer appears to be susceptible of attack by the method of magnetic anisotropy. The method in essence is to determine the anisotropy of the monomer, or of the repeating unit, as may be possible from magnetic and X-ray measurements on relatively simple compounds, and then to interpret the anisotropy of the polymer in terms of specific orientation of the molecular magnetic axes.

Polyethylene terephthalate is promising for this kind of study because of the aromatic groups present in the chain. In the work described below, magnetic susceptibility and anisotropy measurements have been made on the polymer in various stages of molecular orientation and under various conditions of heat treatment. Measurements have also been made on dimethyl terephthalate as the nearest analog to the repeating unit in the polymer.

Experimental Part

Magnetic Measurements.—Susceptibility measurements were made by the Gouy method according to standard procedures.

Anisotropy measurements were made mostly by the second "spin" method of Krishnan, although some measurements were made by his first "oscillation" method. The apparatus, which is the same for both methods, will be described in detail.[3]

---

[1] Present address: General Electric Company, Pittsfield, Mass.

[2] Present address: Bauer and Black, Chicago, Illinois. During the period of this work, at the Rayon Technical Division, E. I. du Pont de Nemours and Company, Inc., Buffalo, N. Y.

[3] Krishnan, Guha and Banerjee, *Phil. Trans. Roy. Soc.* (*London*), **A231**, 235 (1933); **A234**, 265 (1935).

The torsion head was a modified microscope stage. It was graduated in degrees, and could be read to three minutes of arc by use of a vernier. The bearing surface of the graduated torsion head rested on a sturdy ring-shaped brass bearing, which was attached to a brass plate one-quarter inch in thickness. Through the center of the torsion head there was fitted a cylindrical, stainless steel piece which was held in place by a set screw. The quartz fiber suspension was attached to a finely threaded bolt which passed through the axis of rotation of the center piece. By this means the sample could be adjusted to the proper height between the pole pieces of the magnet.

The support for the torsion head, a framework made of one inch angle iron, was bolted to the sturdy table on which the magnet rested. Ample clearance was provided so that the iron members did not affect the magnetic field. Provision for leveling and centering was made in the following manner: a one-quarter inch thick brass plate was supported horizontally on the center of the framework by four leveling bolts. To this was bolted the torsion head assembly; the bolts threaded into the lower plate and passed through relatively large holes in the plate to which the torsion head was attached. The bolt heads were prevented from passing through these holes by washers. By this means the torsion head had sufficient lateral freedom of movement, before the bolts were tightened, to allow for centering. To protect the suspension from drafts, a glass tube, 48 cm. long by 22 mm. o. d. was clamped vertically on the under side of the lower brass plate at the center of the torsion head.

A magnetic field of 5450 oersteds was supplied by a permanent magnet manufactured by The Indiana Steel Products Company.[4] The flat pole-pieces were four inches in diameter and one inch apart. Specifications called for a field uniform to 0.25% throughout a volume of one cubic inch in the center of the gap. The magnet was mounted on a screw-driven carriage powered by a 0.25 horsepower motor. This served the purpose of removing the magnet a distance of 11 inches, which reduced effectively to zero the field surrounding the sample.

The length of the quartz suspension used was 42 cm. The suspension was shellacked to a glass rod (5 mm. by 0.5 mm.) which in turn was shellacked into the end of the center piece bolt in the torsion head. To the lower end of the fine quartz fiber there was shellacked a stout filament of glass about 1 cm. long. In all three instances the flake shellac was melted in place by an electrically heated chromel wire. The fine, almost invisible, quartz fiber used for the suspension was prepared in the manner described by Strong.[5]

Before the magnet was used the field strength and field uniformity were checked. For checking the uniformity of the field at the center of the gap a disc of pure sodium chloride (10 mm. in diameter by 3 mm. in thickness) was attached to the quartz fiber suspension and caused to oscillate about the fiber axis both in and out of the magnetic field. The apparent magnetic anisotropy per gram was 9×10^{-10}, which is very low and indicates a field of high uniformity. The field strength was calibrated with a standard nickel chloride solution, using a sample tube of known dimensions, according to the method described by Nettleton and Sugden.[6] For this purpose an analytical balance was temporarily mounted over the magnet. The nickel chloride solution was analyzed for nickel by precipitating and weighing the nickel as nickel dimethylglyoxime, and its density was determined with a density balance. A field strength of 5430 oersteds was calculated which was in good agreement with the value of 5450 oersteds reported by the manufacturer.

The suspensions were calibrated by either or both of two independent procedures: (a) recording the period of oscillation of an object of known moment of inertia, or (b) using a standard crystal of known magnetic anisotropy. To ensure correct results in determining the magnetic anisotropy of dimethyl terephthalate, both methods were used. Comparison of the two calibration methods is shown in Table I.

For the first method a circular galvanometer mirror was used. It measured 0.0425 cm. in thickness by 0.6312 cm. in diameter, and weighed 0.335 g. The moment of inertia about the diameter as an axis of oscillation is given by $I = mR^2/4$ where m is the mass in grams and R is the radius in centimeters. After the mirror was attached to the end of the suspension with shellac, it was oscillated about its diameter. The torsional constant, C, is given by $C = 4\pi^2 I/T^2$ where T is the period of oscillation. Accurate observation of the period of oscillation was facilitated by use of a galvanometer lamp and scale.

Copper sulfate pentahydrate was convenient to use as a standard crystal in the second calibration procedure, because it readily forms good single crystals. It is most easily suspended with the *c* axis vertical, *i.e.*, with the (*hk*0) faces vertical. Using the reported[7] value of $\Delta\chi = 183 \times 10^{-6}$, the value of the torsional constant may be calculated from the "spin" formula as described later.

Dimethyl Terephthalate Crystals.—Crystals of dimethyl terephthalate were secured by slow evaporation from a 4:1 dioxane–ethyl alcohol solution. Slow evaporation was ensured by grinding the rim of the crystallizing dish flat and covering it with a ground plate of glass. A circular glass plate was set in the bottom of the crystallizing dish so that at least one crystal face would develop perfectly flat. A saturated solution of twice recrystallized dimethyl terephthalate, filtered and then warmed to dissolve any nuclei which might develop during filtration, was poured into the dish, which was then covered and set aside where it would not be disturbed. Within a week or two a number of crystals grew, from which suitable ones were picked. These were washed in alcohol and dried between two pieces of filter paper. The crystals chosen were usually small (5 to 15 mg.) and were, therefore, weighed on a microbalance. Extreme care was used in handling the crystals to prevent contamination.

Dimethyl terephthalate crystallizes in the orthorhombic system and therefore the magnetic axes coincide with the crystallographic axes. The dioxane–ethyl alcohol solution yielded lath-shaped crystals. The orthorhombic unit cell contains four molecules.[8]

In attaching the crystals to the suspension the following procedure was used: the suspension, including the steel centerpiece was laid on a table, with the free end on a glass plate. The stout fiber on the end of the suspension rested on a narrow glass strip cut from a microscope slide, such that both ends protruded over an edge. Adjustment of the crystal to the proper height with reference to the end of the suspension was accomplished by laying the crystal on a glass slide, or two or three coverslips. A bit of orange shellac dissolved in alcohol was applied to the end of the suspension, and the crystal was touched to the glass fiber at the right place by manipulating the glass slide on which the crystal rested. Now that the glass end-piece was stuck to the end of one of the crystal axes, it could be teased into parallel alignment with a piece of wire. For checking the correctness of alignment a very short focal length telescope with a protractor eyepiece was used. The crystal was now left undisturbed for at least four hours to allow the shellac to dry. A final check on the alignment of the crystal was made after the suspension was put in place in the torsion head.

The torsion head was now rotated so that there was zero torsion on the fiber when the magnetic field was applied. The torsion head was then turned through an angle θ such that the crystal would suddenly spin through a large angle. Torsional constant and crystal size were adjusted so that θ

---

(4) The principal advantage of a permanent magnet over an electromagnet for this work is the large price differential.

(5) Strong, "Procedures in Experimental Physics," Prentice-Hall, Inc., New York, N. Y., 1948, p. 205.

(6) Nettleton and Sugden. *Proc. Roy. Soc.* (*London*), **A173**, 313 (1939)

(7) Krishnan and Mookherji, *Nature*, **140**, 896 (1937); *Phys. Rev.*, **50**, 860 (1936); **54**, 533, 841 (1938).

(8) Private communication from E. I. du Pont de Nemours and Company.

was above five complete revolutions at the point where the spin occurred. The anisotropy in the horizontal plane is then given by $\chi_1 - \chi_2 = (MC/mH^2)(2\theta - \pi/2)$ where M is the formula weight, m the mass and H the field.[3]

This procedure determines only the difference between the principal susceptibilities lying in the plane perpendicular to the axis of rotation. Suspending the crystal in succession about the three principal axes of magnetic susceptibility will enable us to determine the values of $\chi_1 - \chi_2$, $\chi_1 - \chi_3$, and $\chi_2 - \chi_3$. In order to calculate the principal susceptibilities we must have another determination. We have $\chi_{\text{average}} = (\chi_1 + \chi_2 + \chi_3)/3$. The average susceptibility was determined on a powdered sample of the dimethyl terephthalate. This was done on a Gouy balance. The principal susceptibilities were then calculated from χ_{average} plus any two of the simultaneous anisotropy equations.

If the magnetic field had been provided by an electromagnet, the equilibrium position of the crystal could have been determined by observing the orientation at which the crystal did not experience any twisting movement on application of the field. A more precise method, and the only method which can be used with a permanent magnet is as follows: The crystal is set approximately at the angle of no torque, and then the angle of rotation of the torsion head in a clockwise direction, θ_c, at which the crystal just spins is determined. The magnetic field is removed, the crystal set at the same approximate equilibrium position, and then the magnetic field is applied again. This time the counterclockwise spin angle, θ_{cc}, of the torsion head is recorded. The average of θ_c and θ_{cc} is the correct angle of spin, θ, from which the equilibrium position of the torsion head is easily calculated. The value $2\,\theta = \theta_c + \theta_{cc}$, after conversion to radians, was used for calculation of the anisotropy.

For finding the anisotropy of dimethyl terephthalate in the *ac* plane it was more expedient to use the "oscillation" method. For this mode of suspension the anisotropy was so low, and therefore the effect of the field so feeble, that it was difficult to judge the equilibrium position with any accuracy. The anisotropy is given by the expression $\chi_1 - \chi_2 = (T_0^2 - T^2)MC/T^2mH^2$ where T and T_0 are the oscillation periods with field on and off, respectively.[3]

Inasmuch as the crystallographic and magnetic axes coincide in the orthorhombic system, the orientations of the crystal axes in the field are given directly, and there is no need to resort to the somewhat tedious determinations necessary for crystals of lower symmetry.

Polyethylene Terephthalate.—Polymer filament samples of various draw ratios were available[9]; they had been drawn at 91°. Draw ratio is the ratio of the final length to the length of the undrawn fiber.

The filaments were made into little bundles or sheaves about 5 mm. long, containing from 20 to 40 fibers, and weighing approximately 10 mg. This was accomplished by winding the filament around a little grooved jig fashioned from a tubing clamp (Fisher Castalloy Hosecock). The filament bundle was tied with two pieces of fine filament, and cut off at the desired length with sharp, small scissors. The bundle and constituent fibers were straightened as well as possible and then a thin solution of glyptal resin in ethyl acetate was applied to the ends. When dry, the tie cords were removed and the sample was weighed. After magnetic measurements were complete, the glyptal was dissolved away and an accurate weighing of the fibers was made. Usually the weight of the adhesive amounted to approximately 0.5 mg.

This complicated procedure was made necessary by the small diameter of the uniformly drawn filaments. There is random orientation of the long chain molecules about the fiber axis, and therefore each filament behaves as a uniaxial crystal with a principal susceptibility along the fiber axis. Thus the magnetic anisotropy is completely determined by suspending the bundle of fibers with the axis of symmetry (fiber axis) horizontal. The "spin" method was used.

For calculation of the principal susceptibilities normal and parallel to the fiber axis, it is necessary to know the average susceptibility of the polymer. This was determined by a Gouy measurement on a cylinder of unoriented polyethylene terephthalate.

Next we consider the relation between magnetic anisotropy and annealing temperature. The temperature runs were carried out in two different ways: (a) the fibers were allowed to shrink, and (b) the fibers were not allowed to shrink. Reasons for this will be discussed later.

In the first case the samples were held together with three tie cords and shellac. The tie cords (5.5X draw ratio) were never removed, since they were required to hold the bundles together during annealing. A room temperature measurement was made, and the quantity $(2\theta - \pi/2)$ so obtained was considered to correspond to the average anisotropy of the sample as previously determined. Subsequent values of the magnetic anisotropy after heat treatment are based on this initial angle of twist. Fortunately, the anisotropy of the 5.5X draw ratio filaments, as used for tie cords, does not change over the temperature range covered. After the room temperature measurement was made, the sheaf of fibers was placed in a small beaker and set in an oven for two hours, which was considered long enough for any significant changes to develop. The temperatures were controlled to ±0.5°. When the sample was removed from the oven it was quenched by setting the beaker in cracked ice. The magnetic anisotropy was measured and then the sample was returned to the oven for another two hours at a different annealing temperature. This process was repeated until the entire temperature range was covered.

For the second temperature run, in which shrinkage was not to occur, the polymer fibers were wound around a grooved brass jig, which was placed in the oven for two hours at the desired temperature. It was necessary to use three or four tie cords to maintain straight alignment of the fibers; for although the fibers cannot contract to any visible extent, they can and do elongate a little at the higher temperatures. After being quenched, the filaments were made into little sheaves stuck together with glyptal. Obviously, separate bundles of the same sample had to be prepared for each different temperature.

Results on Dimethyl Terephthalate

The significant data are given in Table I. The second column gives the torsional constants of the suspensions in c. g. s. units (suspensions often broke). In the third column is given the mode of suspension, *i. e.*, the axis by which the crystal was suspended. When the field was on, the crystal found an equilibrium position: $b \perp$ H means that the b axis was normal to the field in the horizontal plane at equilibrium. The approximate equilibrium reading of the torsion head in degrees is listed in the column headed E. R. The next two columns give the clockwise and counterclockwise spin angle rotations of the torsion head, θ_c and θ_{cc}, respectively, in degrees; and the following column records the value of $(2\theta - \pi/2)$ in radians for calculation of the magnetic anisotropy given in the final column.

As pointed out earlier it was more expedient to use the oscillation method for determining the anisotropy in the *ac* plane; thus, for the last two rows of data we record periods of oscillations with and without the field, T and T_0, respectively. For this mode of suspension there is some uncertainty in finding the equilibrium orientation. This predicament is indicated in the table by a question mark.

---

(9) The polymer samples were generously provided by E. I. du Pont de Nemours and Company.

TABLE I

MAGNETIC ANISOTROPY OF DIMETHYL TEREPHTHALATE

Wt. of crystal in mg.	$C \times 10^4$	Vertical axis	Orientation in field	E. R. in degrees	θ_c in revs. + degrees	θ_{cc} in revs. + degrees	$2\theta - \pi/2$ radians	$-\Delta\chi \times 10^6$
24.0	6.752[a]	*c*	$b \perp$ H	325	24 + 295	24 + 26	311.0	57.2
4.622	1.058[a]	*c*	$b \perp$ H	0	30 256	30 118	384.1	57.5
6.78	9.619[b]	*c*	$b \perp$ H	180	5 201	5 173	16.74	57.3
23.4	6.752[a]	*a*	$b \perp$ H	110	23 296	23 257	295.1	55.6
27.4	168.5[a]	*a*	$b \perp$ H	55	1 143	1 321	14.2	57.0
6.78	9.619[b]	*a*	$b \perp$ H	310	4 392	4 342	60.54	56.2
					T_0 in seconds	T in seconds		
18.2	6.752[a]	*b*	*c* approx. 45 degrees to field?		6.59	5.34		0.13
24.1	16.19[a]	*b*	*c* approx. 45 degrees to field?		5.24	4.42		0.18

[a] Calibrated by oscillating object of known moment of inertia. [b] Calibrated with crystal of copper sulfate.

Averaging the results of Table I, we obtain

$$\chi_b - \chi_a = -57.3 \times 10^{-6}$$
$$\chi_b - \chi_c = -56.3 \times 10^{-6}$$
$$\chi_c - \chi_a = -0.2 \times 10^{-6}$$

and by subtracting the second from the first equation

$$\chi_c - \chi_a = -1.0 \times 10^{-6}$$

which differs from the third equation by only 0.8×10^{-6} unit and therefore proves the data to be self-consistent.

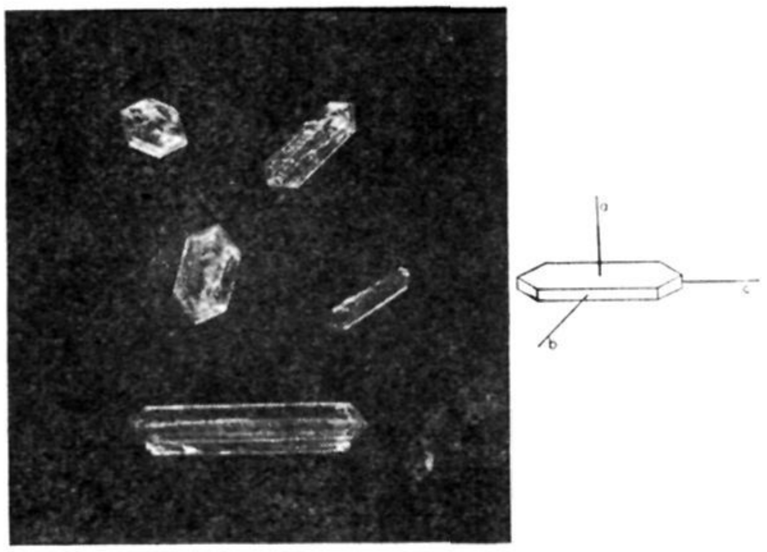

Fig. 1.—Crystals of dimethyl terephthalate, and axis orientation.

It was very difficult to suspend the crystals precisely by the *a* axis, and therefore the results for $\chi_b - \chi_c$ are probably not quite so accurate as the other anisotropies. We shall accordingly use the values of $\chi_b - \chi_a$ and $\chi_c - \chi_a$ in conjunction with the average powder susceptibility to calculate the principal susceptibilities.

For the Gouy determination of the powder susceptibility we find

$$\chi_{\text{average}} = (\chi_a + \chi_b + \chi_c)/3 = -102.7 \times 10^{-6}$$

This is the susceptibility per mole (at room temperature). Hence we calculate the principal molar susceptibilities of dimethyl terephthalate to be

$$\chi_a = -83.5 \times 10^{-6}$$
$$\chi_c = -140.8 \times 10^{-6}$$
$$\chi_c = -83.7 \times 10^{-6}$$

It is seen that, within experimental error, the crystal is magnetically uniaxial with

$$\chi_a = \chi_c = -83.6 \times 10^{-6}$$

Discussion of Results on Dimethyl Terephthalate

It is well known that in many cases it is possible to calculate principal molecular susceptibilities from the principal crystalline susceptibilities and the direction-cosines of the molecules. Unfortunately the X-ray data necessary for making this calculation for dimethyl terephthalate are not yet available.

If the conditions are favorable in the orthorhombic system, the converse procedure of calculating the orientation of the molecule from its molecular susceptibilities and the crystalline susceptibilities can be partially carried out to the extent that we may find the direction of the normal to the plane of the molecule. These conditions are that, in the plane of the molecule $\kappa_1 \doteq \kappa_2$ (where $\kappa_1\kappa_2$ are two of the principal molecular susceptibilities), and that the number of molecules per unit cell is not greater than the minimum required by the symmetry. Let C_{ki} be the molecular direction-cosines in the general tensor expression $\chi_1 = C^2_{ki}\kappa_k$ relating crystalline to molecular susceptibilities.[10] Then

$$\chi_1 = C^2_{11}\kappa_1 + C^2_{21}\kappa_2 + C^2_{31}\kappa_3$$

or for $\kappa_1 = \kappa_2$

$$\chi_1 = (C^2_{11} + C^2_{21})\kappa_1 + C^2_{31}\kappa_3$$

or

$$C^2_{31} = (\chi_1 - \kappa_1)/(\kappa_3 - \kappa_1)$$

and in general

$$C^2_{3i} = (\chi_i - \kappa_1)/(\kappa_3 - \kappa_1)$$

It will be of interest to make such a calculation for dimethyl terephthalate, for comparison of the results with those from X-ray data, when the latter become available.

In order to make such a calculation, we have to assume that the contribution of the ester group to the principal susceptibilities of the

---

[10] Lonsdale and Krishnan, *Proc. Roy. Soc. (London)*, **A156**, 597 (1936).

molecule is the same in all three directions. The validity of such an assumption is open to serious questioning, for Lonsdale[11] has shown that not only carbonate and nitrate groups, but also acetate, carboxylic acid and groups of conjugated double bonds such as occur in oxalic and maleic acids exhibit an abnormally large diamagnetic susceptibility normal to the plane of the atoms constituting the group. The anisotropy of the carbonate and acid groups is about 4 or 5 units per carbon atom. Furthermore, in the case of aromatic molecules with conjugated aliphatic side chains, the magnetic anisotropy is greater than would be expected for the aromatic part of the molecule alone. However, if we wish to make an estimate of the orientation of the aromatic plane of dimethyl terephthalate, we have no choice but to make the above assumption.

The difference between the average susceptibility of dimethyl terephthalate, 102.7 units, and that of benzene,[12] 53.1, is 49.6. Lonsdale[13] gives the mean molecular susceptibility of benzene in the plane of the ring as 32.5 and $|\Delta\kappa|$ between this value and the susceptibility perpendicular to the ring as 61.9. Therefore, $\kappa\perp = 94.4$, since $\kappa\perp > \kappa||$, numerically. Adding the difference, 49.6 to $\kappa\perp$ and $\kappa||$ for benzene, we estimate the three principal molecular susceptibilities of dimethyl terephthalate to be

$$\kappa_1 = \kappa_2 = 82.1,\ \kappa_3 = 144.0$$

The principal crystalline susceptibilities we have found to be $\chi_a = \chi_c = 83.6$, and $\chi_b = 140.8$. Applying the cosine formula we obtain for the angles between the normal to the aromatic plane (κ_3) and the crystal axes

$$\psi_{3a} = \psi_{3c} = 81.0 \text{ degrees}$$
$$\psi_{3b} = 13.1 \text{ degrees}$$

It follows from this calculation that the plane of the molecule, while tipped with reference to all three axes, is roughly parallel to the (010) plane of the crystal. If later work shows that this orientation is not correct, it will probably mean that the ester groups give rise to resonance planes not unlike those shown by the results of Pace[14] and of Gregory and Lassettre[15] on *m*- and *p*-dinitrobenzene.

Results on Polyethylene Terephthalate

The Gouy measurement on a cylinder of unoriented polyethylene terephthalate yielded an average susceptibility of -97×10^{-6} per mole of dimethylene terephthalate. This measurement is probably somewhat less accurate than that performed on the dimethyl terephthalate, which gave a powder susceptibility of -101.6×10^{-6} per mole of dimethylene terephthalate. The two results are considered to be in good agreement.

All fiber samples were suspended with the filament axis horizontal. The unique axis of symmetry assumed an equilibrium position parallel to the field. Some difficulty was encountered in getting uniform fiber bundles. This doubtless accounts for the somewhat erratic results, all of which are shown in Table II.

TABLE II

MAGNETIC ANISOTROPY OF POLYETHYLENE TEREPHTHALATE FIBERS DRAWN AT 91°

Measurements made at room temperature, 25°

Draw ratio X	No. of observations	$-\Delta\chi \times 10^6$ average	Deviation from mean Average ±	Max.
1.0	4	1.04	0.32	+0.37
1.5	4	1.58	.21	+ .33
2.0	3	2.64	.41	+ .76
2.5	3	3.59	.51	− .76
3.0	5	4.52	.50	+ .83
3.5	8	5.90	1.20	+2.16
4.0	3	8.78	0.62	−0.93
4.5	2	18.5	.2	− .2
5.0	3	27.4	.4	− .7
5.5	3	25.0	.2	− .3

When the samples were annealed so that shrinkage could occur, the following observations were made: at 60° there is no perceptible shrinkage. At 75° the samples of draw ratio 1.5X, 2.0X and 2.5X shrink approximately 20 to 30%. Samples 3.0X, 3.5X and 4.0X contract progressively less, the last showing very little shortening. Annealing at temperatures higher than 75° causes no further contraction.

When shrinkage was prevented, the opposite effect is observed for the 3.0X sample at and above 85°. Below 85° no change in length of the fibers was discernible. At the 85° annealing temperature the 3.0X sample shows a barely perceptible stretching along the fiber axis. This elongation is distinctly evident at 95° and becomes increasingly evident as the annealing temperature is raised. In the case of the 5.0X sample there is no detectible change in length of the fiber over the temperature range covered (25° to 145°). All data on annealed samples are shown in Tables III and IV.

TABLE III

MAGNETIC ANISOTROPY OF POLYETHYLENE TEREPHTHALATE *versus* ANNEALING TEMPERATURE.

SHRINKAGE ALLOWED

The anisotropies are expressed as $-\Delta\chi \times 10^6$

Draw ratio	25°	60°	75°	100°	123°	130°	142°	150°
1.5X	1.58	1.58	0.34	0.83	1.23	1.03	1.06	1.26
2.0X	2.64	2.38	0.28	1.20	1.18	1.39	1.44	1.72
2.5X	3.59	3.54	0.93	1.48	1.91	1.00	1.41	1.65
3.0X	4.52	4.24	1.56	0.80	0.98	1.07	0.88	1.40
3.5X	5.90	6.05	2.93	4.72	6.39	5.84	5.75	6.33
4.0X	8.78	9.25	7.02	9.43	11.7	13.2	12.9	15.2
4.5X	18.5	18.2	17.7	18.7	20.9	20.6	21.3	21.5
5.0X	27.4	26.6	26.9	25.1	24.2	24.2	24.6	24.2
5.5X	25.0	25.0	24.7	25.0	24.5	25.0	24.4	24.9

---

(11) Lonsdale, *Proc. Roy. Soc.* (*London*), **A171**, 541 (1939).

(12) Cabrera and Fallenbrach, *Z. Physik*, **89**, 682 (1934).

(13) Lonsdale, *Proc. Roy. Soc.* (*London*), **A159**, 149 (1937).

(14) Pace, Abstracts of Doctoral Dissertations, No. 42, The Ohio State University, 1943, p. 99.

(15) Gregory and Lassettre, THIS JOURNAL, **69**, 102 (1947).

TABLE IV

MAGNETIC ANISOTROPY OF POLYETHYLENE TEREPHTHALATE *versus* ANNEALING TEMPERATURE

No shrinkage. A. Draw ratio, 3.0X

Annealing temp., °C.	Observations	$-\Delta\chi \times 10^6$, average	Deviation from mean Average, ±	Deviation from mean Max.
25		4.52		
60	4	4.32	0.64	−1.02
65	4	3.08	.38	+0.68
70	4	3.91	.79	−0.94
75	4	3.70	.48	−0.88
85	4	4.61	.10	+0.19
95	4	6.80	.39	−0.73
105	4	7.95	.87	+1.57
120	4	8.05	1.03	+2.0
130	4	9.83	0.97	+1.5
145	2	11.4	0.1	+0.1
	B.	Draw ratio, 5.0X		
25		27.4		
60	3	26.7	0.5	−0.9
65	6	24.6	.3	−0.7
70	5	24.7	.4	+0.9
75	2	24.5	.2	−0.2
108	3	25.1	.7	−1.0
145	3	24.6	.1	−0.2

Discussion of Results on Polyethylene Terephthalate

The discussion of magnetic anisotropy as a function of draw ratio and of temperature is conveniently approached from the concept of three phases, each stable within a certain range: first, a phase consisting of a rather immobile random molecular arrangement stable at low temperatures and low draw ratios; second, a phase of more mobile polymer segments stable at higher temperatures and low draw ratios; and third, a phase stable at high draw ratios and in which the polymer chains are arranged more nearly parallel. At low draw ratios increased annealing temperature would then lead to a limiting anisotropy characteristic of the second phase, whereas at some intermediate draw ratio the third phase becomes stable and increased annealing temperature leads to alignment of chains and hence to increased anisotropy.

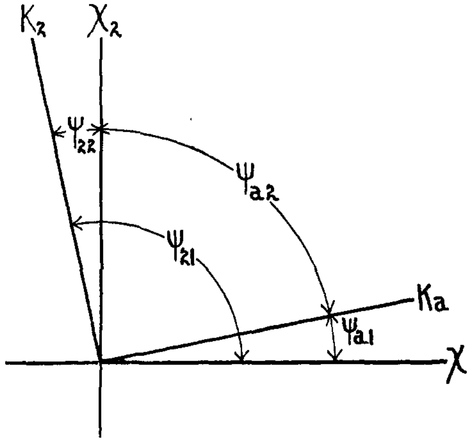

Fig. 2.—Relation of fiber and magnetic axes.

Orientation of the Molecular Chain.—If we assume that the monomer units are magnetically identical with dimethylene terephthalate corrected for two magnetically isotropic hydrogen atoms, the principal molecular susceptibilities of dimethyl terephthalate and the magnetic anisotropies of polyethylene terephthalate may be used to calculate the average orientation of the aromatic plane (and thus the molecular chain) to the filament axis. This calculation must wait for the completion of X-ray studies on dimethyl terephthalate, but the method will be indicated.

The fiber possesses uniaxial symmetry presumably because there is random orientation of the aromatic planes about the fiber axis. In the hypothetical case where the long axis of all monomer units and all the aromatic planes are parallel to the filament axis, the susceptibility normal to the filament axis equals the average of the molecular susceptibility perpendicular to the aromatic plane and that in the plane normal to the fiber axis, *i. e.*

$$\chi\perp = (\kappa_1 + \kappa_3)/2 = \kappa_a$$

and

$$\chi|| = \kappa_2$$

For this case the set of cosine equations reduces to

$$\chi\perp = \chi_1 = C^2_{a1}\kappa_a + C^2_{21}\kappa_2$$
$$\chi|| = \chi_2 = C^2_{a2}\kappa_a + C^2_{22}\kappa_2$$

With the aid of Fig. 2 it is seen that

$$\psi_{22} = \psi_{a1} = \psi,\ \psi_{a2} = 90° - \psi, \text{ and } \psi_{21} = 90° + \psi$$

Therefore

$$C^2_{a1} = C^2_{22} = \cos^2\psi$$

and

$$C^2_{21} = C^2_{a2} = \sin^2\psi$$

From the relations above it is easily shown that

$$\cos 2\psi = (\chi_1 - \chi_2)/(\kappa_a - \kappa_2)$$

where ψ is the angle which the aromatic nucleus makes with the filament axis.

Magnetic Anisotropy *versus* Draw Ratio.—The data in Table II show that there is a linear relation between anisotropy and draw ratio for values of the latter up to 3.0X, and that the increase in anisotropy with draw ratio is relatively small. Beyond this value, in the neighborhood of 4.0X, the magnetic anisotropy begins to increase very rapidly with increasing draw ratio through an apparent[16] maximum of 27.4 anisotropy units at 4.0X. Extrapolation of both sections of the curve (Fig. 3) locates this critical point at 3.8X.

---

(16) We say *apparent* maximum because the 5.5X sample was not strictly comparable to the others, having been drawn in two stages, namely 4.0X at 93° and 1.4X at 190°.

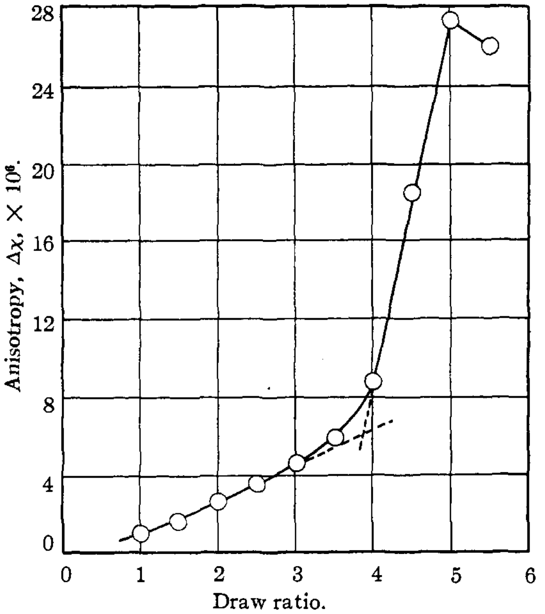

Fig. 3.—Anisotropy *vs.* draw ratio.

These results may be interpreted in the following way: As the amorphous polymer is subjected to increasing tensile stress, the chains tend to straighten out and the segments tend to become more perfectly aligned relative to one another. This process of unkinking the chains reduces the distance between the constituent groups of adjacent chains to the point where short range van der Waals forces begin to be effective. At about 3.8X these forces become so strong that it requires but little more externally applied force in the form of stretching to cause the segments to snap into positions of minimum potential energy. In all likelihood the polar ester groups make a large contribution to the van der Waal's forces, and thus we might look upon the large increment of magnetic anisotropy as due to a sudden alignment of the polar groups. In the region of high and preferred orientation (4.0X to 5.0X) the fibers should tend to become crystalline, that is, there should be a number of crystallites, separated by amorphous regions, distributed at random along the length of the fiber. This apparently agrees with the inferences from observations on mechanical, optical and X-ray properties of the polymer.[8,17–19] However, none of these physical properties pertaining to the crystallinity and close packing of the chains shows a more pronounced change in properties than the plot of magnetic anisotropy. It is clear that in the magnetic anisotropy we have a sensitive means for determining changes in orientation of a magnetically anisotropic polymer molecule.

Magnetic Anisotropy *versus* Annealing Temperature.—The annealing curves (shrinkage allowed) present certain features on which we shall next focus attention. First, for all filaments except those of high draw ratio there is a decided drop in anisotropy near 65°. The wider spread of temperature points in Figs. 3 and 4 does not define this temperature so closely as Fig. 5. The second order transition temperature[8] for the amorphous polymer is stated to be 67°. Thus, we see that the drop in magnetic anisotropy probably corresponds to the second order

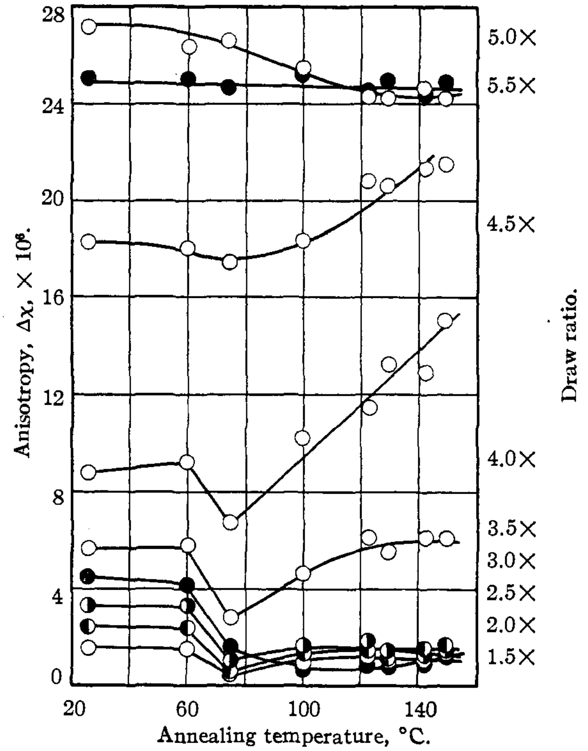

Fig. 4.—Anisotropy *vs.* annealing temperature for nine different draw ratios. Shrinkage allowed.

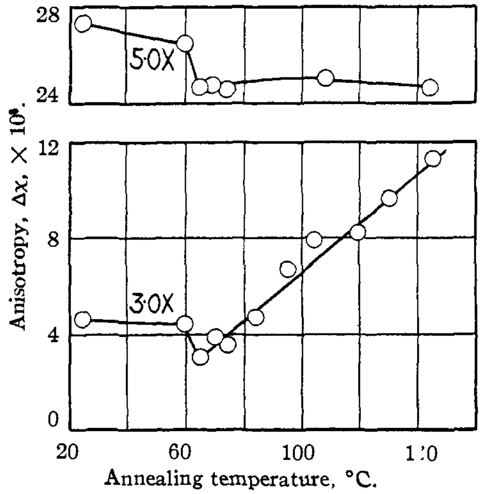

Fig. 5.—Anisotropy *vs.* annealing temperature for two different draw ratios. No shrinkage.

(17) Astbury and Browne, *Nature*, **158**, 871 (1946).

(18) Whinfield, *ibid.*, **158**, 930 (1946).

(19) Hardy and Wood, *ibid.*, **159**, 673 (1947).

transition. Also, at this point, it will be recalled, fibers 1.5X through 4.0X showed contraction. This is in agreement with the theory of rotation about primary valence bonds. The fibers are under no restraint and therefore the segments are free to rotate and assume a random, kinked, orientation.

Second, it is noted that filaments of low draw ratio (through 3.0X) exhibit only a slight increase in anisotropy after the initial drop; but that samples of higher draw ratio, with the exception of 5.0X and 5.5X, show an increase in orientation at the higher annealing temperatures. The 3.5X fiber reaches its initial value; the 4.0X and 4.5X filaments considerably exceed their initial anisotropies, rising to 15.2 and 21.6, respectively. The 5.0X drops from 27.4 to 24.2, and the 5.5X sample remains nearly constant at 24.6. There appears to be a trend, in the case of filaments which are initially relatively well ordered, to attain an optimum value of orientation, which (if we focus our attention on the 4.5X, 5.0X and 5.5X samples) seems to be in the neighborhood of 22 to 25 magnetic anisotropy units.

These results may be interpreted as follows: Filaments which are relatively well ordered will experience an initial slight decrease in ordering owing to rotation about valence bonds at the second order transition temperature. As more energy is supplied the various groups rotate or oscillate, but the packing is still rather close and the alignment is good, so that it is easier for the groups to pull into positions of still better alignment (and lower potential energy) than it is for them to overcome close range forces and curl up. Therefore, with longer periods of annealing at higher temperatures the molecular chains become more highly oriented. The high magnetic anisotropy of the 5.0X sample does not necessarily mean that it is initially more crystalline than the others, but only that the aromatic nuclei are more nearly parallel to the fiber axis. The fact that its magnetic anisotropy decreases with annealing to about the same final value as that of the 5.5X fiber would indicate that such is the case, and that the final value of 24 to 25 anisotropy units more nearly approximates conditions of crystallinity and minimum potential energy. See, however, footnote 16.

In the case of fibers of low draw ratio and, therefore, low initial orientation, it will be observed that the final magnetic anisotropy for all is approximately the same, 1.3 units. This is probably some statistical average random orientation consistent with the shape of the molecule and the external shape of the filament, (it will be observed that the supposedly completely random 1.0X sample is not quite isotropic), or it may simply be a shape anisotropy due to a slight non-uniformity in the field.

We now ask ourselves: if the molecular chains experience rotation about the primary valence bonds and curl around themselves, when free to do so, with consequent contraction, what will happen if the shrinkage is prevented, or at least severely restricted? The answer to this question appears in Fig. 5. The 3.0X sample, after a slight initial decrease of anisotropy at 65°, shows a steady increase in orientation until at 145° it has attained a value almost three times greater than the initial value. It will be recalled that when shrinkage occurred the magnetic anisotropy of this sample dropped to a low value and remained there. In the present case the molecules could not curl up when rotation set in and there was, therefore, no alternative but to straighten out, with consequent ordering and stretching. This is exactly what happened. At 85° a slight elongation was noticeable and at higher annealing temperatures this elongation was more pronounced. For the 5.0X filaments there was no visible elongation or contraction and, as before, the initial orientation and packing are such that the short range forces are strong enough to pull the chains in slightly more favorable orientation when internal rotation or oscillation sets in.

Just why, even in cases where there is an ultimate increase in magnetic anisotropy, there should be an initial drop in anisotropy at the second order transition point is not clear. It might be that the chains have to acquire a certain amount of energy of internal motion, with consequent disordering, before the groups can begin to move into more favorable positions.

Acknowledgment.—It is a pleasure to acknowledge the support of E. I. du Pont de Nemours and Company in connection with this work. The authors wish especially to express their appreciation to members of Pioneering Research, Rayon Technical Division, in Buffalo, New York.

Summary

Principal magnetic susceptibilities have been determined for crystalline dimethyl terephthalate and for polyethylene terephthalate. The anisotropy of the polymer has been studied as a function of mechanical treatment (draw ratio), and as a function of temperature. The results have been interpreted in terms of molecular orientations.

EVANSTON, ILLINOIS RECEIVED DECEMBER 6, 1948