

4. In the case of dodecylamine hydrochloride the conductivity rises in the third range in spite of greatly increased viscosity.

5. The values of Λ_0 and l_c have been determined from the experimental data.

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Effects of Heat, Solvents and Hydrogen-bonding Agents on the Crystallinity of Cellulose Esters

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Recent investigations¹⁻⁴ have sought to elucidate the nature of the solid state of cellulose and its derivatives. X-Ray studies have shown the presence of crystalline components, and the existence of "amorphous" or disorganized inter-crystalline matter has been inferred. The importance to physical properties of the balance between the crystalline and non-crystalline phases in these polymers is increasingly evident. However, relatively little progress has been made in determining the configurations of amorphous or disordered states or the circumstances causing them. The present work aims to indicate an important type of disorder which can be produced in cellulose esters by heat treatment, and to investigate with X-ray diffraction the crystallizing effects of various agents on these disordered systems.

The behavior of the synthetic linear polyamides previously noted⁵ is strictly parallel to that of the cellulose polymers. The concepts of coexisting crystalline and disordered states and of kinetic mobility of chain segments in solid polymers appear to have general application.

Experimental

Materials.—The cellulose triacetate^{5a} had a solution viscosity of $(\eta_{sp}/c)_{c \rightarrow 0} = 0.564$, at 25.0° in chloroform. (Viscosity values are from extrapolation to $c = 0$ of the linear concentration dependence of η_{sp}/c .) The cellulose tributyrates^{5a} was of $(\eta_{sp}/c)_{c \rightarrow 0} = 0.757$, 25.0°, in chloroform, and the cellulose acetate-butyrate, $(\eta_{sp}/c)_{c \rightarrow 0} = 1.929$, 25.0°, in acetone. The cellulose esters were obtained from the Eastman Kodak Company and all were white, pure finely-divided flakes.

(1) W. A. Sisson, *Ind. Eng. Chem.*, **30**, 530 (1938); *Chem. Rev.*, **26**, 187 (1940).

(2) H. Mark, *Chem. Rev.*, **26**, 169 (1940).

(3) P. H. Hermans, *J. Phys. Chem.*, **45**, 27 (1941).

(4) K. Hess and C. Trogus, *Z. physik. Chem.*, **B15**, 157 (1932).

(5) C. S. Fuller, W. O. Baker and N. R. Pape, *THIS JOURNAL*, **62**, 3275 (1940).

(5a) The designation "triesters" means that technical class of esters, and does not imply stoichiometrically complete esterification. Tests indicate, however, that the acyl value was within 1% of complete esterification.

Heat Treatment.—Samples allowed to solidify near their melting points were formed to uniform cross-section by extruding ribbons under slight pressure into a small steel mold open at one end and maintained a few degrees below the melt temperature. Since the molten polymer occupied nearly the total volume of the system, no appreciable oxidation occurred by air exposure. The samples were dried and maintained so during the whole treatment. The triacetate was fused at 240° under slightly elevated pressure, the tributyrates at 180° and the acetate-butyrate at 210°. These may be regarded as about the normal melting points of the compounds. Melts for the quenching experiments were maintained at about 250° for the triacetate and acetate-butyrate, and about 190° for the tributyrates. Samples were quenched from their melts at both 20° and -75°, with apparently equivalent results. The quenched samples discussed below were prepared by rapid transfer of molten pellets to a heavy brass plate of high heat capacity maintained at -75° with dry-ice. A second plate, likewise cooled, was immediately applied above the sample and was separated from the lower plate by shims yielding samples of 0.069 cm. thickness except that this thickness was increased to 0.086 cm. for the crystallization rate measurements on the tributyrates.

For the annealing experiments, the dry quenched samples were mounted rigidly on the X-ray collimating insert, photographed with filtered copper X-radiation for a given constant period, at constant voltage in the tube, and were then inserted in a Pyrex tube in a thermostated electric furnace, at selected temperatures below their softening or deforming points. The tube contained aluminum granules, on which the metal insert was placed, so that the high heat capacity and conductivity of its environment warmed the small cellulose ester strip quickly. This was important for short annealing times at high temperatures. Likewise, the position of the strip with respect to the incident beam was kept constant for successive exposures during the annealing, as required for the intensity comparisons. The annealing was always in a reduced, dry hydrogen atmosphere, and the prolonged heating times noted for some of the esters produced no sign of decomposition. Samples were cooled to room temperature before exposure and were stored in desiccators when not mounted in the camera.

Solvent Treatment.—Quenched ribbons of standard, equal thickness were suspended at 25° in a vapor concentration of representative solvents produced by their equilibrium vapor pressure at the given temperature. Treatment times were insufficient to cause noticeable

swelling or softening of the sample. The samples were freed from solvent before X-ray exposure.

Water Treatment.—Water was selected as a typical and common hydrogen-bonding agent, and the results discussed below were obtained from immersion of the dry, quenched samples in water at 100° for the given times. They were dried before irradiation and were, again, of constant thickness, so that diffusion rate was minimized in the comparisons.

Results and Discussion

Quenching and Annealing.—Figure 1A (the figures are from Debye-Scherrer patterns sectioned for compactness) illustrates the high crystallinity of cellulose triacetate allowed to solidify near the fusion temperature, compared to the much more random disposition of the chains, especially around their long axes, when quenched at -75° (Fig. 1B). The pattern 1A contains rings with d , Å., values agreeing closely with those of Hess and Trogus⁶ for cellulose triacetate II. The Fig. 1B pattern compared with unpublished oriented diagrams contains a heavy diffuse inner ring corresponding to disorganized lateral spacings including d values of 10.45, 8.58 and 6.70 Å. Then occurs a sharper intermediate ring of $d = 5.09$ Å., probably the second order of the chain repeating distance, and a very broad outer ring, $d = 3.11$ Å., again showing lateral disorder. Thus, the solid resulting from the quenching may be considered as much more amorphous than that from the slow cooling. Of course, in the latter, current concepts forbid an aggregate composed only of minute crystallites, but approve crystalline areas bounded by disordered regions through which, indeed, a given chain can wander, in a convoluted path, to take up again another crystalline state for part of its length. The pattern of Fig. 1A would then result from a maximum crystallite content and a minimum volume of intervening, disordered chains. The crystallites grow as close together as possible in the solid of highest crystallinity (if the long chains had short enough relaxation times to extend completely and become parallel from the melt, the crystals could grow without any interrupting amorphous regions). Interpretation of the diffraction results is probably little complicated by uncertainty of whether line breadth variations result independently from changes in crystallite size or in total amorphous content, since they seem to be concurrent phenomena.

Clearly, different mechanical properties occur for the quenched samples compared to the crys-

talline. While the evidence is not so striking as in the polyamides because of the rigidity and high interaction of the cellulose chains, the sample corresponding to Fig. 1A was both harder and stronger than that of 1B. Since widely different states of a cellulose ester can evidently be produced, the question arises of their significance for the technically important changes of properties with time in plastic bodies, such as those of plasticity, elasticity and dimensions. At least one rate process which can contribute to these changes appears in Figs. 1, C, D, E and F and in the succeeding figures. Apparently, the disordered chains of Fig. 1B acquire sufficient kinetic mobility in the solid state, from thermal energy, to rotate into progressively more organized average states. Crystallization thus occurs considerably below the melting point. Now, the sort of intermolecular action overcome in this annealing is a proportion of that determining the mechanical nature of the plastic, and thus the temperatures necessary to effect the rearrangement in a given time elucidate directly the relative magnitudes of the interchain forces present in, for example, a series of thermoplastic cellulose derivatives. Subsequently, the effect of simple liquids containing plasticizer groups will be discussed as analogous to the influence of temperature on the given structure.

Interchain Forces.—The patterns on Fig. 1 from the annealed samples emphasize the high intermolecular forces commonly attributed to cellulose triacetate, since ninety-five hours at 150° produces no detectable crystallization, while eight minutes at this temperature causes extensive chain rearrangement in cellulose tributyrates (see Fig. 2). The high temperature coefficient of chain segment rotation into the lattice indicated by partial crystallization in thirty minutes at 200° (Fig. 1D), and by a sharply defined pattern at 225° (two hours is not a minimum time, in Fig. 1F) also reflects these forces. We regard this temperature coefficient as an activation energy involved in the absolute rate process⁷ of chain sections surmounting the potential barriers imposed by their neighbors, and settling eventually into the potential minima (and minimum free energy) of the crystal lattice. Of course, this rate process involves also a significant entropy term: the surrounding chains must, in general,

(6) K. Hess and C. Trogus, *Z. physik. Chem.*, **B5**, 161 (1929).

(7) S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

be in special momentary positions for a given one to move over its barriers. These factors are considered more quantitatively for the tributyrates, but the differences noted above for the two triesters are significant. Since the acetyl and butyryl groups have about the same polarity, and the dispersion forces^{8,9} in the butyryl group are actually larger, the large decrease in intermolecular action from the triacetate to the tributyrates may be attributed back to the cellulose residues. The longer acyl residue appears to force the skeletons further apart, laterally.¹⁰ Thus, the dispersion forces between the polarizable cellulose chains, whose potential decreases as $1/r^6$, are critically affected by small increases in distance, such as the two extra carbon atoms of the butyryl radical contribute compared to the acetyl. Of course, chain dipoles also interact, and their potential falls off as $1/r^3$, in the "prying apart" of longer acyl residues. These considerations with the results of Figs. 1 and 2 explain the pronounced modification, essentially an internal plasticizing, produced by the longer acyl substituents in cellulose esters. The increase in interchain distance necessary for flexibility and toughness (decreased modulus) may be accomplished by dispersing an agent of low molecular weight among the chains, or by separating the chains with longer lateral substituents.¹¹ Cellulose tributyrates is as regular a structure as cellulose triacetate; however, the X-ray results show a considerably greater ease of chain rotation in the former case. This again indicates the importance of the separation of the cellulose residues.

Superposed on the forces noted above are the hydrogen bonds present in the partial esters commonly used. Their effect is strikingly shown in Fig. 3. Comparison of Figs. 3A and 3B shows that the mixed ester, acetate butyrate, is highly crystalline on slow cooling but very amorphous when quenched. The acetate butyrate studied has 0.2 mole of residual hydroxyl groups per pyranose ring, along with about 0.6 mole of butyryl and 2.2 moles of acetyl. It might thus show high interaction like cellulose triacetate with contributions from a hydrogen-bonded derivative, reduced by the chain separation induced by the butyryl. The relative disposition of the acyl radicals along

the chain is probably quite homogeneous.¹² These high forces strongly stabilize the disordered states obtained by quenching, and Figs. 3C and 3D show that the compound, unlike the triesters, cannot be annealed below its softening point. Since the melting point is below the temperature found necessary to cause rotation of the triacetate chains in the solid (Fig. 1), Fig. 3 does not prove whether the hydrogen-bonding or the predominance of acetyl residues prevents solid state crystallization of the quenched acetate butyrate, but later discussion of Fig. 7 indicates that hydrogen-bonding is important in preventing the chain motion requisite for annealing. This leads to an interesting speculation on the minimum length of the crystallizing segment in the esters. On the average, a hydroxyl group occurs on every fifth glucose unit. If the rotating section were shorter than this, the residual hydrogen-bonding would not be expected to affect the annealing of the acetate butyrate, contrary to other indications. The results indicate that cellulose derivatives with residual hydroxyls capable of hydrogen-bonding form, like the polyamides, amorphous configurations on quenching which are stable at ordinary temperatures for long periods.

Interplanar Spacings and Degrees of Order.—Table I lists the interplanar distances appearing on the Debye-Scherrer patterns of the various quenched and unquenched esters. Sodium chloride dusted on the specimen served as a direct calibration for the d values. Identification of the Debye-Scherrer reflections as interchain spacings required fiber patterns. Well oriented diagrams of the esters have been obtained, and that of the triacetate II has been reported.¹³ The first inner ring appearing on all of the accompanying figures, sharp and strong from the crystalline states and diffuse but intense from the quenched states, may be regarded as a lateral spacing, which increases with the length of the substituted acyl group.¹⁰ Interestingly, the value in Table I for the acetate-butyrates, 10.83 Å., is between the triacetate and tributyrates, but nearer the triacetate, as might be expected from its 2.2 moles of acetyl compared to 0.6 mole of butyryl per ring unit. This averaging of lateral distance, which reflects one sort of chain interaction, agrees with the the gradation in properties as the mixed ester composition is varied. The middle diffuse ring

(8) F. London, *Z. Physik*, **63**, 245 (1930); *Z. physik. Chem.*, **B11**, 222 (1931).

(9) H. Margenau, *Rev. Mod. Phys.*, **11**, 1 (1939).

(10) J. J. Trillat, *Compt. rend.*, **197**, 1616 (1933).

(11) C. R. Fordyce and L. W. A. Meyer, *Ind. Eng. Chem.*, **32**, 1053 (1940).

(12) H. M. Spurlin, *THIS JOURNAL*, **61**, 2222 (1939).

(13) K. Hess and C. Trogus, *Z. physik. Chem.*, **B9**, 160 (1930).

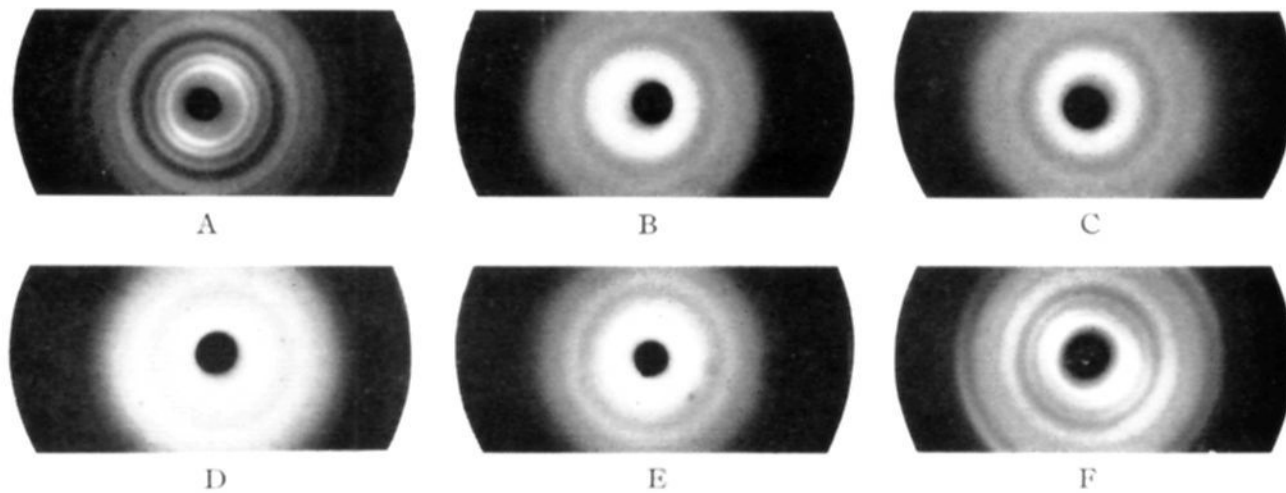


Fig. 1.—X-Ray patterns of cellulose triacetate showing effect of heat treatment: A, solidified near melting point; B, quenched at -75° ; C, (B) annealed 95 hrs., 150° ; D, (B) annealed 30 min., 200° ; E, (B) annealed 2 hrs., 200° ; F, (B) annealed 2 hrs., 225° .

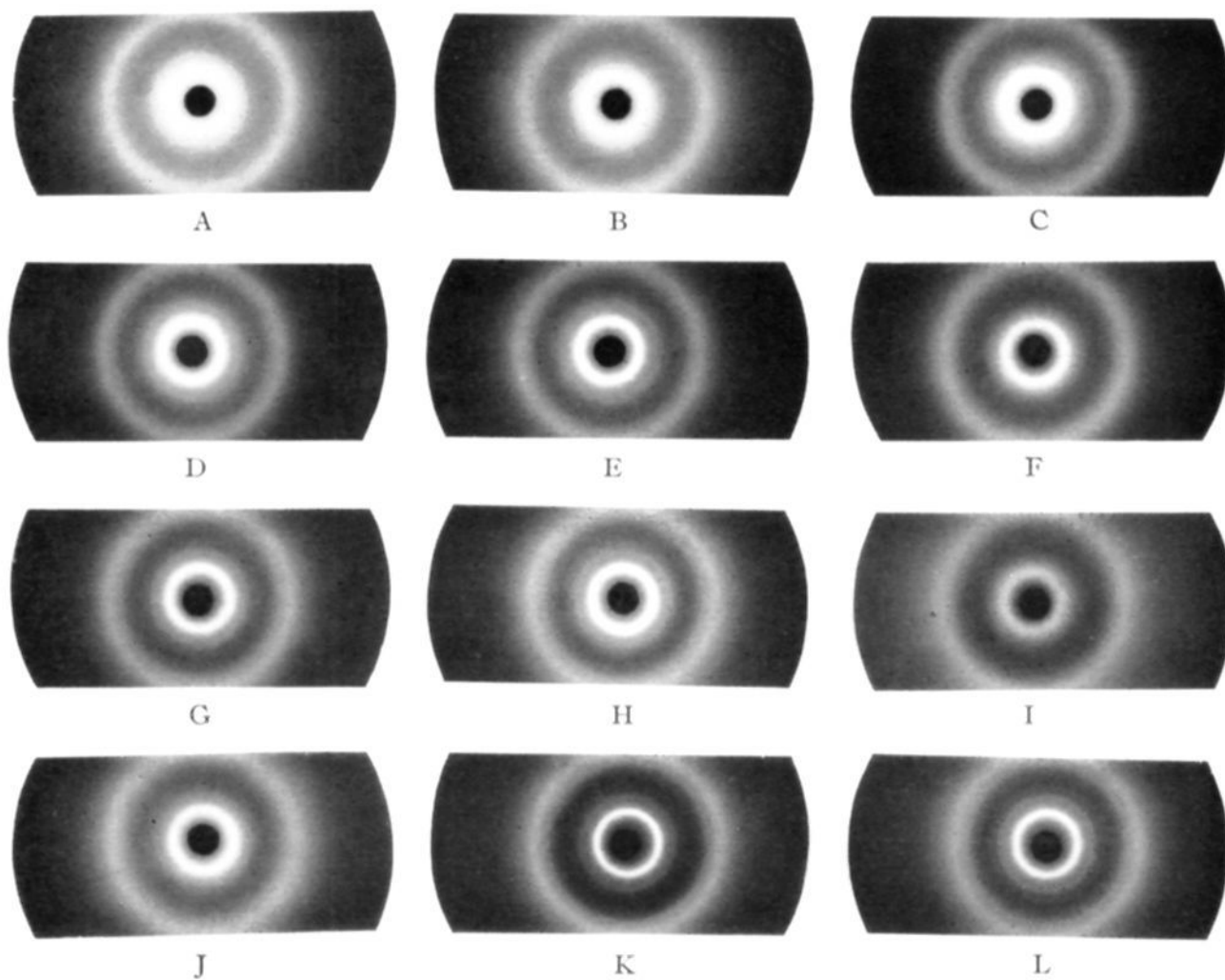


Fig. 2.—X-Ray patterns of cellulose tributyrate showing rate of annealing as a function of temperature: A, quenched at -75° . Samples of (A) were then annealed as follows: B, 600 min., 100° ; C, 1200 min., 100° ; D, 3000 min., 100° ; E, 6960 min., 100° ; F, 20 min., 120° ; G, 40 min., 120° ; H, 150 min., 120° ; I, 5 min., 150° ; J, 8 min., 150° ; K, 20 min., 150° ; L, 30 min., 150° .

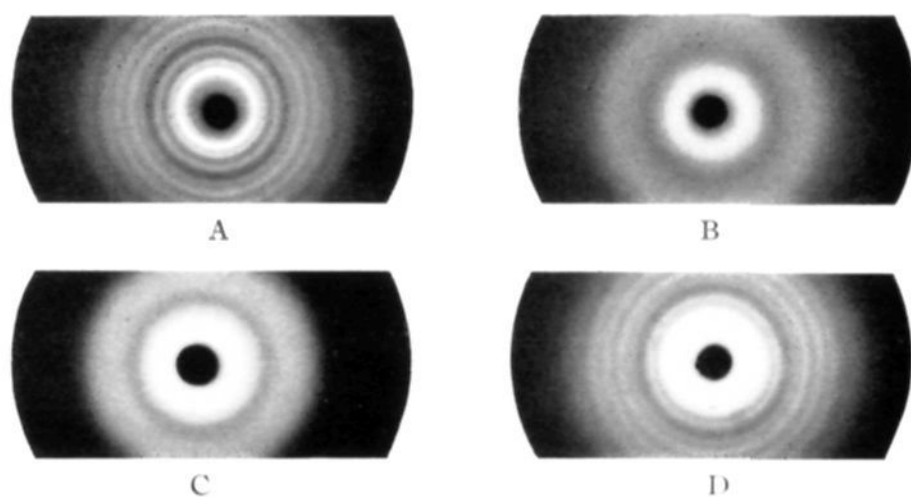


Fig. 3.—X-Ray patterns of cellulose acetate-butyrate showing effect of heat treatment: A, solidified near melting point; B, quenched at -75° ; C, (B) annealed 20 hrs., 160° ; D, (B) heated 2 hrs., 195° , sample softened.

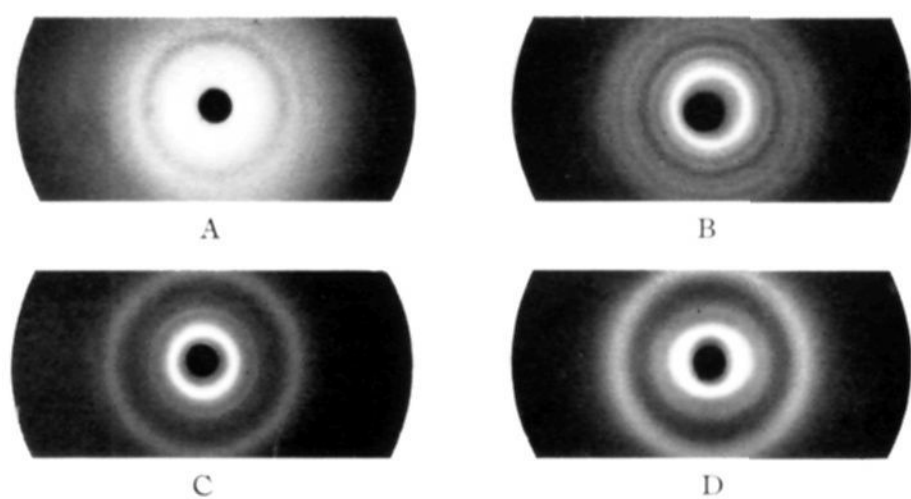


Fig. 6.—X-Ray patterns showing effect of solvent vapors at 25° on quenched cellulose esters: A, cellulose triacetate, 4 hrs., chloroform; B, cellulose acetate-butyrate, 2 hrs., acetone; C, cellulose tributyrate, 8 min., chloroform; D, cellulose tributyrate, 10 min., acetone.

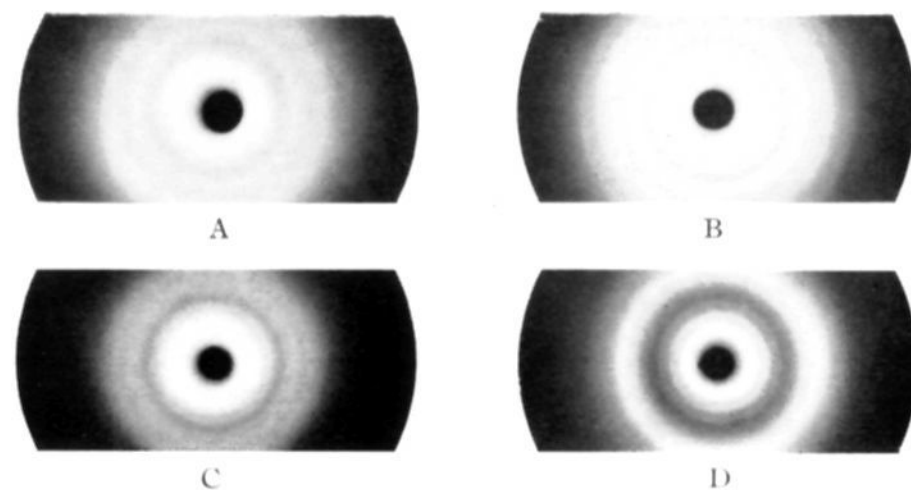


Fig. 7.—X-Ray patterns showing effect of water at 100° on quenched cellulose esters: A, cellulose triacetate, 3 hrs.; B, cellulose triacetate, 5 hrs.; C, cellulose acetate-butyrate, 3 hrs.; D, cellulose tributyrate, 1 hr.

TABLE I
INTERPLANAR DISTANCES IN THE CELLULOSE ESTERS

The identifications of the rings as M, meridian, L, layer-line, and E, equatorial, spacings are from the fiber patterns.

| Ring | Cellulose triacetate <i>d</i> , Å. | | Cellulose acetate-butyrate <i>d</i> , Å. | | Cellulose tributyrate <i>d</i> , Å. | |
|------|------------------------------------|----------|--|----------|-------------------------------------|----------|
| | Crystallized | Quenched | Crystallized | Quenched | Crystallized | Quenched |
| 1 | 10.35 E | 10.45 | 10.83 E | 10.93 | 12.25 E | 13.35 |
| 2 | 8.40 E | 8.58 | 8.68 E | | 9.73 E | |
| 3 | 6.53 E | 6.70 | 6.88 E | | 7.95 E | |
| 4 | 5.24 M | 5.09 | 5.58 E | | 6.65 E | |
| 5 | 4.86 L | | 4.94 L | 5.09 M | 5.69 E | |
| 6 | 4.18 E | | 4.32 E | | 4.89 E | |
| 7 | 3.75 E | 3.91 | 3.86 E | 4.21 | 4.32 L | 4.45 |
| 8 | 3.28 M | | 3.45 M | | | |
| 9 | 3.01 | | 3.27 | | | |
| 10 | 2.57 | | 2.59 | | | |

appearing on the quenched patterns (see Figs. 1B, 2A and 3B) seems to correspond to a repeating distance in the chain molecule, comprising two pyranose rings. However, in the highly crystalline and also in the oriented diagrams, a repeating distance provided by planes perpendicular to the long axes of the molecules does not appear for the tributyrate; layer-line but not meridian reflections result from *annealed* oriented samples. However, planes perpendicular to the chain axes appear in the triacetate and acetate butyrate, as noted from sharp and detailed fiber patterns. Further, in the quenched tributyrate the outer ring (which is also the "middle" ring discussed here, since none appears beyond it, unlike the other quenched esters) has a *d* value of 4.45 Å., and not the 5.09 Å. (which corresponds to the 10.3 ± 0.5 Å. generally found for the repeating distance in cellulose and most of its derivatives of the other two in Table I. However, the distance from the tributyrate layer-line measurement is 5.08 Å., probably the second order of the chain repeating distance. Thus it appears that in quenched cellulose triacetate and the particular acetate-butyrate of Table I, the chains align so that planes from the terminal atoms of repeating units are perpendicular to the long molecular axis. In the tributyrate, reduced interchain attraction and the bulkiness of side chains seem to prohibit these planes. The outermost rings on the triacetate and acetate-butyrate appear also to arise from side spacings.

The diffuse rings discussed above reflect, thus, the disordered array of chains. They cannot with certainty be called amorphous, even so much as, say, liquid benzene. For instance, it is significant that long chains in a quenched or liquid polymer provide fixed distances along the chain through lengths which may well be ap-

proximately parallel to each other in small groups of adjacent chains. Thus, a given scattering group or atom has neighbors fixed at definite distances on either side along its chain. This sort of partially fixed structure differs therefore from low molecular assemblies. All of the quenched patterns show a ring related to chemical repeating unit distance (with the modifications noted above for the tributyrate). Then they show diffuse rings of averaged interchain spacings, and the numerous features of the crystallized diagrams emphasize the ability of the pyranose rings to generate new planes when they are precisely disposed laterally by annealing. A more detailed analysis would be required to decide from the new features which appear the angles of rotation or distances of shift required for the solid state crystallization. That such displacements are considerable is suggested by the discussion below on the temperature coefficient of the solid state rearrangement of cellulose tributyrate.

Crystallization Rate of Cellulose Tributyrate.—Figure 2 shows the relative rates of crystallization of quenched cellulose tributyrate at 100, 120, and 150°. Samples were mounted on the X-ray insert and kept under constant conditions through a series so that the intensities produced are strictly comparable.¹⁴ The most serious variation was in emulsion thickness. The patterns of Fig. 2 were photometered through a radius with a Zeiss microphotometer of high sensitivity and stability. The resulting curves of Fig. 4 show the development of new features and the general sharpening as the chains rearrange in the solid to the stable crystalline configurations. Although quantitative half-width measurements may be made from these data, the theory of their interpretation is not yet satisfactory. The concept of specific chain dis-

(14) For details, see R. Fricke, *Z. Elektrochem.*, **46**, 641 (1940).

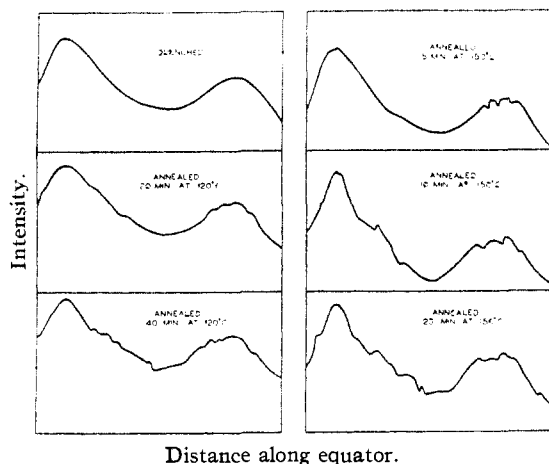


Fig. 4.—Microphotometer curves showing development of features on x-ray pattern by annealing cellulose tributyrate.

placements applies to interpretations of plastic properties as recently discussed by Gloor.¹⁵ The energetics of these displacements determine largely the strength, tendency to flow, plasticizer content needed for toughness, low temperature brittleness, etc., of the material. From Fig. 2 it is seen that while twenty minutes at 150° are required to cause high crystallinity in the quenched sample, one hundred and fifty minutes are necessary at 120° and at least 6960 minutes at 100°. In Fig. 5 is plotted the logarithm of the time in minutes required to produce a given height of the photometer peak appearing for the first new feature beyond the innermost ring, on annealing, against the reciprocal of the absolute temperature of the annealing. The two sets of points are for two-fold different heights, indicating different extents of the "reaction." The peak height was taken as the distance from the intensity maximum (as on Fig. 4) down parallel to the ordinate of the line tangent to the curve showing the rapid decline of background scattering around the intense inner ring. Evidently the points for the three temperatures do not form the straight line expected for a simple rate process. However, from Eyring's theory of absolute reaction rates,⁷ the slopes of lines in Fig. 5 may be regarded as E/R , where E is the activation energy for the chain motion, in calories per mole, and R is the gas constant. Then, the activation energy for the motion necessary to crystallize a mole of cellulose tributyrate units lies between 23,000 and 35,000 calories. This is a high figure and agrees with ideas of the stiffness of the cellulose

(15) W. E. Gloor, *J. Applied Physics*, **12**, 420 (1941).

chain. It is two to three times the energy required for a comparable process in the polyamides.^{5,16} Any significance which may be attached to the non-linearity of the lines connecting the respective points in Fig. 5 stems from the probability that the apparently higher activation energy at the lower temperatures includes a contribution from the work required to expand the solid to allow chain rotation. At the high temperatures, the solid would, of course, be normally more expanded.

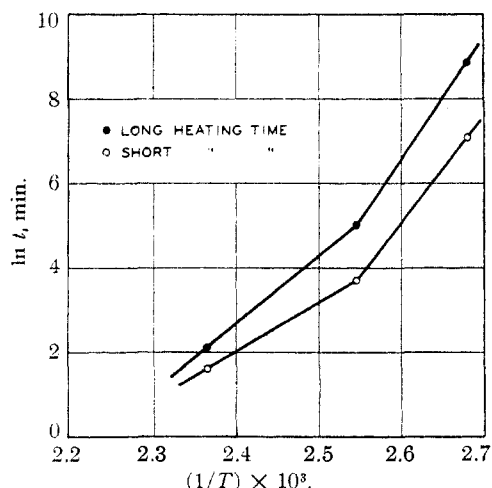


Fig. 5.—Temperature coefficient of the solid state crystallization rate of quenched cellulose tributyrate. The times are those required to reach a given intensity of a single ring; the upper points represent approximately twice the intensity of the lower ones, and hence longer heating times.

Segment Action in the Solid State.—These preliminary results do not define the average size of the cellulose tributyrate section which moves in the solid. However, they exclude the chains from moving as single units, because they would require several-fold 30 kcal. per mole. The results do agree with the segment theory of melting points in chain polymers.^{16,17} Unpublished thermal studies from these Laboratories on linear polymers, such as time-temperature curves, show clearly that the fusion of the crystallites at the observed melting point of the polymer is an equilibrium process by thermodynamic criteria. Hence, the breakdown of the crystallites determines the melting point of the polymer, but the crystallites contain few complete molecules, but rather, segments.

Effect of Solvents.—Figure 6 represents the effect of solvent vapors at 25° on the quenched

(16) Unpublished results.

(17) Preliminary ideas were given in ref. 5.

cellulose esters whose patterns have been shown in previous figures. Wide technical use of cellulose ester films has stimulated inquiry into the influence of the solvents in casting the solids, especially regarding final flexibility. Mathieu¹⁸ observed changes in the sharpness of X-ray patterns of nitrocellulose films from variations in concentration of the solution and the temperature of its evaporation. Films dried at 70° appeared much more crystalline than those made at 20°. This prompted Mathieu to remark that "heat facilitates the natural tendency of the chains to dispose themselves in a regular manner, that is, a kind of annealing takes place." The present work on melts and films well confirms Mathieu's observation on the latter, and indicates the ease of extending the current concepts to cellulose nitrate. Likewise, Jones and Miles¹⁹ proposed that amorphous constituents conferred flexibility on films, while Sheppard and Newsome²⁰ suggested that small crystallites also produced flexibility. Previously, the idea of variation in crystallite size by the rate of precipitation of cellulose acetate from solution had been noted by Mark.²¹ Spence²² extended similar ideas in a study of birefringence and concluded that "good" solvents, like ethylene chlorohydrin for cellulose triacetate, gave more brittle films of higher crystallinity than a "poor" solvent like, say, chloroform.

Figure 6 represents a direct method of studying the effect of solvents on the crystallinity of the esters. A given ester may be quenched to a disordered state. Then, exposure to solvent vapor causes solvation of the chains, permitting the rotation at ordinary temperatures. The extent of resultant crystallization, measured by diffraction patterns after removal of the imbibed solvent, suggests whether the solvent is "good" or "poor," and whether the crystallinity of the film will be high or low. Thus, Fig. 6A agrees that chloroform is a "poor" solvent for cellulose triacetate, while comparison of Figs. 6C and 6D show that it is a "better" solvent for cellulose tributyrate than acetone; acetone films of the tributyrate are less crystalline than those from chloroform. Evidently, from Fig. 6B, acetone is a good solvent for the mixed, partial acetate-butyrate. Hence, the ideas of heat annealing,

(18) M. Mathieu, *Trans. Faraday Soc.*, **29**, 122 (1933).

(19) G. G. Jones and F. D. Miles, *J. Soc. Chem. Ind.*, **52**, 251T (1933).

(20) S. E. Sheppard and P. T. Newsome, *ibid.*, **56**, 256T (1937).

(21) H. Mark, *Kolloid-Z.*, **53**, 40 (1930).

(22) J. Spence, *J. Phys. Chem.*, **45**, 401 (1941).

solvent vapor crystallization, and crystalline-amorphous ratio fit in well with the principles of cellulose ester film and lacquer practice. We have not answered why one solvent permits more complete chain motion and solid state crystallization than another but this behavior of the fine structure (*i. e.*, relative positions of the molecules) may be definitely related to the properties of the films formed. Complications of retention of the solvent, phase separation on evaporation and free energy of solvation, enter the complete explanation.

Effect of Water.—Figure 7 emphasizes the importance of residual hydrogen-bonding in the esters. It was remarked concerning Fig. 3 that the acetate-butyrate partial ester could not be annealed in the solid. If these high interchain forces contributed partly by the residual hydroxyls are turned to advantage by bonding with a softening agent which lowers the modulus of the polymer, a useful plastic is formed. Gloor¹⁶ has proposed that the bonding of plasticizers to partial acetates increases with increasing hydroxyl content, and that the bonding forces are similar to those tending to hydrate cellulose acetate. These views seem reasonable from the results of Fig. 7. The strong polar, hydrogen-bonding agent water facilitates chain motion and crystallization for all of the compounds, including the triesters. But, strikingly, Fig. 7C shows considerable crystallization after three hours at 100° in water for the quenched acetate-butyrate which was unaffected after twenty hours at 160° dry (Fig. 3C) and which could not be annealed dry below its softening point. Water may serve as a model of a simple plasticizer (its effects on commercial plastics are well known) for the considerations of this report. With the triesters, its dipoles help to neutralize those of the acyl groups, and its swelling action forces the chains apart slightly and thus reduces the critical dispersion forces accented in previous paragraphs. With the partial esters, water splits interchain hydrogen-bonding in forming its own bonds with cellulose hydroxyls, and likewise exerts a swelling action. Figure 7 demonstrates, also, how moisture can easily provide the chain motion requisite for the dimensional changes so characteristic in cellulose plastics. Hence, the elimination of warpage and other distortion caused by moisture will require modification of the molecular structure so that the interchain forces are weakened. There

is then less tendency for the molecules to seek any one permanent configuration.

General Interpretation of Patterns.—The diffraction patterns and factors varying them found in this and previous⁵ reports may reflect phenomena occurring widely in more complex polymeric systems. X-Ray investigations on cellulose, starch and proteins, for example, have commonly yielded diagrams varying under the conditions of study. However, these conditions were either uncontrolled or were not accounted for in the observed result. Thus, the investigations of Katz,²³ and recently of Bear and French,²⁴ on starch, those of Mathieu¹⁸ on nitrocellulose and of Kubo²⁵ on the effect of glycerol at high temperatures on hydrate cellulose may involve the ordering of the molecules as discussed above. Likewise, the rearrangements involved in the denaturation of proteins by heat, light and chemical agents may be related to the breaking of hydrogen bonds and the improved ordering of chains or molecular segments as found for the linear polyamides.⁵ This is speculation, but affirmatively, a sharpening of Debye-Scherrer rings occurs on protein denaturation.²⁶

Summary

Various states of molecular organization in the solid from crystalline to disordered have been produced in cellulose triacetate, cellulose acetate-butyrate (0.6 mole butyryl, 0.2 mole residual hydroxyl, per chain unit) and cellulose tributyrate, by quenching and annealing. X-Ray analysis shows high crystallinity and order on solidification a few degrees below the melting point, while quenching leaves chain sections apparently locally parallel but randomly rotated about their long axes. The high interchain forces

(23) J. R. Katz and J. C. Derksen, *Z. physik. Chem.*, **A150**, 100 (1930).

(24) R. S. Bear and D. French, *THIS JOURNAL*, **63**, 2298 (1941).

(25) T. Kubo, *Kolloid Z.*, **93**, 338 (1940).

(26) M. Spiegel-Adolf and G. C. Henny, Atlantic City Meeting of the A. C. S., Sept., 1941.

of cellulose and its derivatives preserve these configurations at ordinary temperatures and their amorphous quality modifies the physical properties of the solids. However, diffraction patterns show the chains acquired sufficient kinetic energy on heating at much less than the melting point to move into the stable, lattice array. Direct evidence of this chain motion and its dependence on the nature and extent of the acyl substituents suggests the mechanism of molecular displacements occurring in certain plastic, elastic and dimensional behavior of the polymers.

The temperature coefficient of the rate of solid-state annealing of cellulose tributyrate, determined by microphotometering the X-ray patterns, was interpreted as an activation energy. It is two to three times the value for similar motion in the solid of zigzag chains (as polyamides), and reflects the stiffness and interaction of the chain skeleton. Comparison of the solid-state crystallization rates for the three typical esters indicates that the most significant structural modification by longer acyl residues is separation of the cellulose chains. The large polarizability, and thus dispersion forces, of the latter cause the high modulus of the solid derivative.

Solvent vapors facilitate chain motion in the quenched solids, and produce, at, say, 25°, final degrees of crystallinity which reflect the suitability of the solvent for flexible film formation.

Water as a typical hydrogen-bonding agent seemed to neutralize dipoles in the triesters and permitted increased chain motion, but its effect was most marked where it could bond with residual hydroxyls. Its behavior may be traced as that of a simple plasticizer.

The results relate directly to the old question of whether linear macromolecules are extended or kinked in the unoriented crystalline state, for crystalline arrays of molecules having approximately the degree of extension they had in the liquid have been produced.

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