

Modification of the Fine Structure of Cellulose by Halogen and Heat Treatments*

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Synopsis

Treatment of various celluloses such as cotton, sulphite, and sulphate pulp with bromine water brings about profound changes in the fine structure of the fiber. Depending on the conditions of the treatment and on the nature of the cellulose, increases or decreases in the accessibility of the cellulose are observed, indicating crystallization and decrystallization processes. In the case of bleached sulphate pulp, similarly to rayon previously studied, an initial decrystallization precedes the crystallization step. These changes were determined by the IR method, which was correlated previously to the bromine accessibility method. They are accompanied by highly significant changes in moisture absorption. The crystallization proceeds according to first-order kinetics with respect to the concentration of the less-ordered regions (LOR) of the cellulose. The rates of crystallization for the various celluloses varied in a range of 4 orders of magnitude. The activation energies of the bromide induced crystallization were found for all celluloses to be in the range of 10–15 kcal/mol, as compared to 30–40 kcal/mol obtained upon crystallizing the same celluloses by heating in the temperature range of 180–200°C. These values correspond to those of solvent and thermal crystallizations of poly(ethylene terephthalate), indicating the similarity between the crystallization mechanisms of the two polymers.

INTRODUCTION

In previous reports from this laboratory, some of the fine structural changes occurring in cotton and rayon, upon treatment with bromine water, were discussed.^{1–3} The changes were observed at pH values below 2, in which the elementary bromine is the predominant moiety.^{4,5} The bromine molecules are preferentially sorbed on the glycosidic oxygen in the less-ordered regions (LOR) of the cellulose.⁶ The sorption was shown to be reversible and to proceed according to the Langmuir-type isotherm for 16 various celluloses, including several varieties of native, hydrolyzed ramie as well as regenerated celluloses.¹ From the Langmuir-type isotherms, accessibility values were computed which were found to correlate by straight-line relationships with crystallinity indices.¹ The accessibility method developed on the basis of the above data was found to depend on the bromine concentration and temperature. At concentrations of bromine below 0.02 mol/L, sorption times of up to 2 h and at 25°C, the reproducibility of the method was within 1–2%. At higher concentrations and temperatures, the accessibility values were lower, indicating the occurrence of a crystallization process. This crystallization process in cotton was further evidenced by increased XRD indices and by decreased moisture regain and dyeability.¹ It was shown that the crystallization proceeded according to first-order kinetics with regard to the concentration of the LOR of the cellulose and with

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regard to the bromine concentration.² The reaction rate increased with temperature, and activation energies in the range of 10–15 kcal/mol were calculated for the temperature range of 10–40°C. These activation energy values are in the range of values obtained in diffusion processes. They differ greatly from activation energies of 31–46 kcal/mol obtained by Hatakeyama et al.⁷ from infrared data for the nucleation or incipient crystallization of an amorphous cellulose by heating in dry nitrogen at 94–150°C. Since the results of Hatakeyama et al. pertain to a primary nucleation producing very small crystallites which could not be detected clearly by X-ray diffraction and since they were unable to measure rates of crystal growth, it is not clear whether the activation energies obtained can be ascribed to thermal crystallization of cellulose. In order to compare the thermal crystallization to the bromine-induced crystallization, it is necessary therefore to investigate the kinetics of the crystallization processes on similar substrates. Such data are presented in the present study.

While the crystallization of cotton cellulose appears to be governed by relatively simple first-order kinetics at a given concentration of bromine, in the case of rayon fibers a decrystallization process occurs in the initial stages of the interaction with the bromine water solution, possibly simultaneously with the crystallization.³ The decrystallization phenomenon is evidenced by an increase in accessibility, by a decrease in the XRD crystallinity index, and by an increase in moisture regain. The rates of these both opposing phenomena were found to depend greatly on the orientation of the fibers and consequently on the distances between the chains, since higher orientations are usually indicative of a higher density of packing of the molecules in the polymer. The probability of the chains aligning themselves to positions conducive to the formation of bridges by the bromine molecules will decrease by larger distances between the chains. The crystallization rate will decrease since longer times will be necessary for the chain segments to approach each other. The effect will be similar to decreasing the concentration of reactants in a homogenous reaction. A similar influence of orientation was observed previously in this laboratory in the case of pyrolysis of rayon.^{8,9}

The kinetics of the two opposing reactions was investigated for high modulus rayon, and formulae were derived in which their rate constants and activation energies were calculated.³ While no full explanation for the decrystallization could be given, it was suggested that the hydrophobic bromine molecules disrupt the van der Waals links existing in the cellulose. Such links, according to Warwicker et al.,¹⁰ hold the cellulose chains together in sheets, which in turn are linked to each other by hydrogen bonds. The disruption of the van der Waals links will produce defects in the crystalline regions and decrease the order in the polymer. The extent of decrystallization will depend on the accessibility of these links to the bromine, which in turn may differ from cellulose to cellulose and may vary with temperature and bromine concentration. The decrystallization phenomenon with bromine was observed hitherto with a number of rayons,² while it did not appear in the case of cotton. It is of considerable interest to establish whether such a decrystallization phenomenon is limited only to regenerated celluloses. In the present report, several additional native celluloses, e.g., Acala SJ-1 cotton, bleached sulphite, and sulphate pulps are investigated.

EXPERIMENTAL

Acala SJ-1 cotton fibers, grown in Israel, bleached Acala 4-42 cotton fabric, supplied by ATA Textiles Co. Ltd., Kfar Ata, Israel, commercial bleached sulphite pulp, supplied by American-Israeli Paper Mills, Hadera, Israel, and commercial bleached kraft pulp, supplied by International Paper Co., Stirling Forest, New York, were used in the present study.

The cotton fibers were purified by the method described by Conrad¹¹ and used in previous studies of this institute.^{12,13} Samples of the pulps of 10 g each calculated as oven dry were disintegrated in a laboratory blender in water, filtered and suspended in previously prepared bromine water solutions at a liquor ratio of 1:100 in closed brown vessels, glass-stoppered, and shaken in a platform shaker immersed in thermostatic bath for various time intervals. After the predetermined time of shaking, the bromine water was decanted, and the pulp was washed several times by dilution and filtered, washed, and air dried.

The cotton fabrics were treated similarly except that instead of disintegrating they were cut into 1-2-mm-long pieces.

The treatments in chlorine water were carried out in a similar way. The fibers were suspended in chlorine water prepared by acidifying a known concentration of sodium hypochlorite with an excess of hydrochloric acid so as to yield a pH of 1.

The heat treatments were carried out in a continuous curing oven, produced by Renz AG, Zurich. The samples were placed on a platform which moved through the oven at a controlled speed.

The moisture regain was determined according to the ASTM method D 885.¹⁴

The accessibility of the cellulose samples was calculated from the IR crystallinity indices determined according to the method of Nelson and O'Connor¹⁵ from the ratio between the intensities of the two peaks at 1429 cm^{-1} and 893 cm^{-1} . The Perkin-Elmer 257 spectrophotometer was used. The pellets were made from 2 mg of ground fibers (Wiley mill, 20 mesh) and 300 mg of KBr, dried in an oven at 115°C for 2.5 h. The mixture of the KBr with the pulp fibers was kept in a desiccator over P_2O_5 . The accessibility of the cellulose was calculated using the linear correlation between the IR crystallinity indices and the accessibility by the bromine method, described previously.^{1,2}

RESULTS AND DISCUSSION

Bromine Water Treatment of Acala SJ-1 Cotton

In Table I and Figure 1 the change in accessibility of Acala SJ-1 cotton, upon treatment with bromine solution, is described. It is evident that in the first 6 min a slight increase in the accessibility from 29.2% to 30.9%, accompanied by a parallel increase in moisture regain from 9.45% to 9.62%, occurs. This increase, although significant, is much smaller than the increase observed previously under similar conditions in the case of high modulus rayon, e.g., from 32% to 42% (in accessibility) in 5 min at 25°C³ and in textile rayon from 48% to 75% in 23 h.² The rapid rate of the decrystallization in the case of cotton is understandable considering the closeness of the packing of the macromolecular chains, which is similar to that of the highly stretched high modulus rayon. The small extent

TABLE I
Bromine-Induced Changes in Accessibility of Acala SJ-1 Cotton^a

Time (min)	Accessibility (%)	Moisture regain (%)
0.0	29.2	5.45
1.0	29.2	9.45
2.5	29.2	9.52
4	30.2	9.53
5	30.2	9.62
6	30.9	9.60
8	30.9	9.50
10	28.0	9.15
15	25.0	9.03
30	22.0	8.69
60	13.0	8.55
120	7.03	8.33
180	4.64	8.12

^a Temp = 25°C; concn of Br₂, 0.17 mol/L; concn of cotton, 10 g/L; pH 2.

of the decrystallization might indicate a relatively low concentration of accessible van der Waals linkages in the cotton.

From the data in Table I, the first-order rate constant of the crystallization, as expressed by the decrease in accessibility, was calculated. In this calculation, the initial accessibility was taken as 30.9, i.e., the maximum point of Figure 1, and the measured time at this maximum, e.g., 6 min, was taken as the starting corrected time, $t_{\text{cor}} = 0$. The value of the rate constant found by linear regression analysis was $1.84 \times 10^{-4} \text{ s}^{-1}$ with a coefficient of correlation (r) of 0.99. It is significantly different from the value of 5.71×10^{-5} obtained previously for Acala 4-42 cotton under analogous conditions.²

Bromine Water Treatment of Bleached Sulphite Pulp

In Table II and Figure 2 the fine structural changes induced in bleached sulphite pulp upon treatment in bromine water solutions are described. While no significant changes occur at 25°C in 0.17 mol/L solution, after a treatment of 5 h, at 40°C the accessibility of the pulp increased from 60% to 62% during the first 5 min and slowly began to decrease. It reached 47% accessibility after 5 h and 38% after 24 h. At 32°C, the accessibility increased only to 61% after 3 min and decreased to 50% after 5 h and 45% after 24 h.

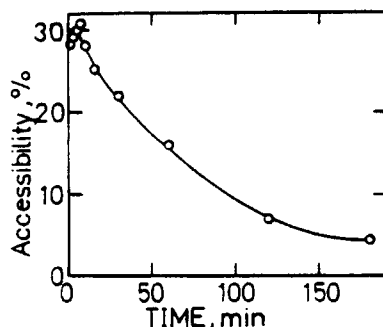


Fig. 1. Change in accessibility of Acala SJ-1 fibers upon treatment with 0.17-mol/L Br₂.

TABLE II
 Bromine-Induced Changes in Accessibility of Bleached Sulphite Pulp^a

Temp (°C)	Time (min)	Time, cor (min)	Accessibility (%)	$\ln [a/(a-x)]$	Moisture regain (%)
25	0		60		8.8
	300		59		8.8
32	0		60		8.8
	1		61		8.8
	3		61		8.8
	5		60		8.8
	10	0	61		8.5
	15	5	60	0.01653	8.3
	30	20	58	0.05043	8.25
	60	50	57	0.06782	8.25
	120	110	56	0.08552	8.0
	180	170	52	0.15963	8.0
40	300	290	50	0.19885	8.0
	1440	1430	45	0.30921	7.6
	0		60		8.8
	1		62		
	3	0	62		
	5	2	61	0.01626	8.7
	10	7	58	0.06669	
	60	57	55	0.1198	
	120	117	53	0.1568	
	180	177	51	0.1953	
300	297	47	0.2769	7.9	
1440	1437	38	0.4895	7.1	

^a Concn of Br₂, 0.17 mol/L; concn of pulp, 10 g/L; pH 2.

As shown in Table II, the moisture regain also decreased significantly with the decrease in accessibility. The rates of crystallization at 32°C and 40°C were found to be $3.1 \times 10^{-6} \text{ s}^{-1}$ ($r = 0.87$) and $5.0 \times 10^{-6} \text{ s}^{-1}$ ($r = 0.92$), respectively. While the maximum in accessibility observed for the sulphite pulp is similar to that of the Acala SJ-1 cotton and occurs in a similar time span, the rate of the subsequent crystallization is by 2 orders of magnitude lower. This rate resembles the rates observed for textile rayon fibers, likewise having a high initial accessibility.²

Bromine and Chlorine Water Treatment of Bleached Sulphate Pulp

In Table III and Figure 3, data on the behavior of bleached sulphate pulp in bromine solutions are given. The most significant finding is that the accessibility increased in the first 10 min to a much higher degree than that found previously

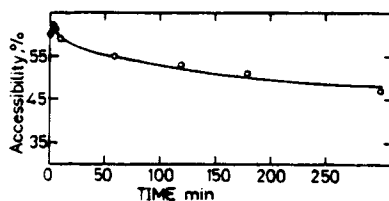


Fig. 2. Changes in accessibility of bleached sulphite pulp upon treatment with 0.17-mol/L Br₂; 40°C.

TABLE III
Bromine-Induced Changes in Accessibility of Bleached Kraft Pulp^a

Temp (°C)	Time (min)	Time, cor (min)	Accessibility (%)	$\ln [a/(a-x)]$	Moisture regain (%)
25	0.0		63		11.54
	3		70		11.85
	10	0.0	72		11.73
	60	50	70	0.282	
	180	170	69	0.0426	11.78
	1440	1430	65	0.1023	
	4320	4310	53	0.3064	11.32
	10403	10398	54	0.2877	11.32
40	0.0		63		
	1		69		
	3		72		
	5		74		
	10	0.0	74		
	15	5	71	0.0414	
	30	20	71	0.0414	
	60	50	72	0.0136	
	180	170	72	0.0274	
	300	290	69	0.070	
	1440	1430	64	0.1452	

^a Concn of Br₂, 0.17 mol/L; concn of pulp, 10 g/L; pH 2.

for sulphite pulp and for cotton. At 25°C the accessibility increased from 63% to 70% in 3 min and to 72% after 10 min. Thereafter, a very slow decrease in accessibility started which reached the original level only after about 30 h. After 3 days of bromine treatment an accessibility of 53% was obtained.

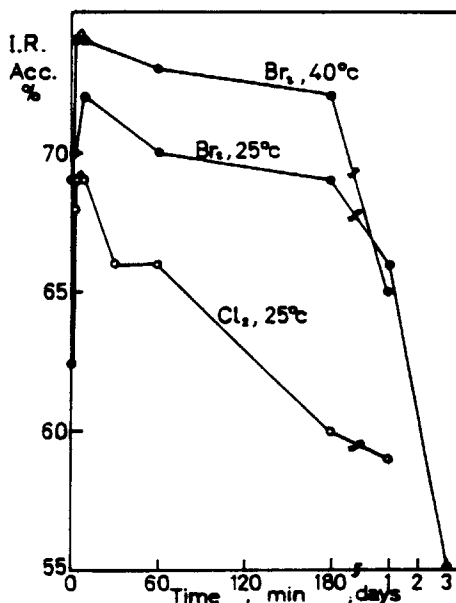


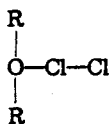
Fig. 3. Accessibility vs. time of treatment of bleached kraft pulp with 0.17 mol/L of Br₂ and 0.1 mol/L of Cl₂.

At 40°C both the rates of decrystallization and of crystallization increased, and the maximum accessibility of 74% was reached already after 5 min. The rates of crystallization at 25°C and 40°C were calculated by the method of least squares to be $5 \times 10^{-7} \text{ s}^{-1}$ ($r = 0.86$) and $1.44 \times 10^{-6} \text{ s}^{-1}$ ($r = 0.93$), respectively, i.e., significantly lower than in the case of the sulphite pulp.

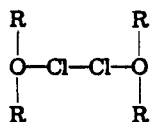
As can be seen in Table III, the moisture regain of the original pulp was 11.54, which is high compared to the sulphite pulp. The initial increase in regain to 11.80 and the subsequent decrease to 11.32 were low relative to the change in accessibility. These changes in moisture regain are considerably smaller than in the case of the sulphite pulp.

In Table IV some preliminary data are shown on the changes in the accessibility of the bleached sulphate pulp upon treatment with Cl_2 solutions. It is evident that the behavior in chlorine is basically similar to the behavior in bromine. A maximum of 69% accessibility was obtained after 5 min. The crystallization, however, started earlier than in the case of bromine and its first-order constant at 25°C, i.e., $1.5 \times 10^{-6} \text{ s}^{-1}$ for chlorine is considerably higher than for bromine. Continuation of the chlorine treatment for a longer time than 24 h was not practical, since the degradation of the pulp was too pronounced and it lost its fibrous character. This is not surprising in view of previous results from this laboratory, which showed that the oxidation of cellulose by chlorine is much more rapid than by bromine and that a considerably higher number of aldehyde groups are formed by this oxidation along with ketone groups and accompanied by a much higher degree of degradation as compared to bromine oxidation.¹⁶

While no systematic data are available on the sorption of chlorine on cellulose, such a sorption was demonstrated to occur as a first stage, preceding oxidation.¹⁶ It is likely therefore, that the mechanism of crystallization by chlorine is identical to the case of bromine, i.e., the formation of an additional compound between chlorine and the glycosidic oxygen



as well as of interchain linear halogen-molecule bridges between two glycosidic oxygens of adjacent chains:



Such linear bridges were observed before by X-ray studies of a 1,4-dioxanbromine 1:1 crystalline compound.¹⁷ Intermediate addition compounds between chlorine and the anomeric oxygen during the oxidation of cellulose model compounds were assumed before.¹⁸⁻²⁰

The halogen-oxygen bridges bring about an alignment of the chains in the LOR by bringing them together and orienting them parallel to each other. This alignment may involve a considerable number of chains. The bridges are destroyed upon reduction or washing out of the halogen, but the chain alignment

TABLE IV
Chlorine-Induced Changes in Accessibility of Bleached Kraft Pulp^a

Time (min)	Time, cor (min)	Accessibility (%)	$\ln [a/(a - x)]$
0		63	
3		68	
5		69	
10	0.0	69	
30	20	66	0.0445
60	50	66	0.0445
180	170	60	0.1398
1440	1430	58	0.1737

^a Temp = 25°C; concn of Cl₂, 0.1 mol/L; concn of pulp, 1%; pH 2.

may persist for a time span sufficient for the formation of strong hydrogen bonds which constitute nuclei for crystallization and subsequently of new crystalline regions.

The above results demonstrate that the sulphate pulp behaves upon treatment with halogens in a unique way, which appears to be intermediate between rayon^{2,3} and sulphite pulp.

The information available at present does not allow us yet to explain the differences between the behaviors of the two pulps. It is not clear whether the differences in the structure of the native wood fibers or the different pulping and bleaching systems used in the two pulps are responsible for the different behavior. It is clear, however, that the decrystallization phenomenon is not inherent to the cellulose II structure. It appears to be connected with the mode of packing of the macromolecules, the extent of the van der Waals linkages, and their accessibility to halogen under the experimental conditions used.

One of the possible reasons for this difference may reside in the presence of

TABLE V
Heat-Induced Changes in Accessibility of Cotton

Temp (°C)	Time (min)	Accessibility (%)	$\ln [a/(a - x)]$	Moisture regain (%)
180	0	32.2		
	1	31.9	0.00094	7.92
	3	28.5	0.122	7.69
	5	25.1	0.249	7.53
	7	23.4	0.319	7.50
	10	21.7	0.395	7.30
	13	20.0	0.476	7.01
	190	1	31.9	0.0093
3		23.5	0.311	7.50
5		19.2	0.517	7.00
7		16.3	0.681	6.63
10		10.9	1.083	6.40
200	1	31.9	0.0093	7.92
	3	18.3	0.565	6.91
	5	14.8	0.777	6.50
	7	9.0	1.275	5.75
	10	4.6	1.946	5.28

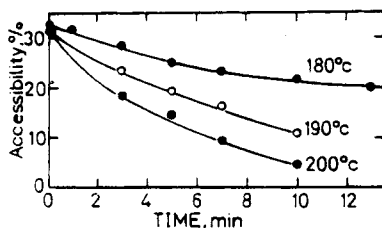


Fig. 4. Change in accessibility of Acala 4-42 cotton upon heating at several temperatures.

the residual lignin in the sulphate pulp. If it is assumed that some of this lignin resides inside the LOR, then it may become more difficult for the bromine to form the bridges between the neighboring chains and align them. Thus the crystallization will be slowed down. Since the lignin is being brominated under the present experimental conditions,²¹⁻²³ it may serve as a relatively effective barrier to the penetration of the bromine molecules into the cellulose structure. A considerable slowdown in moisture absorption and a highly significant decrease in swelling was observed on bromination of wood.²⁴ This may also explain the small changes in moisture regain observed above (see Table III).

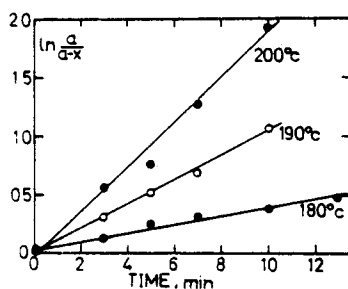


Fig. 5. Kinetics of thermal crystallization of Acala 4-42 cotton.

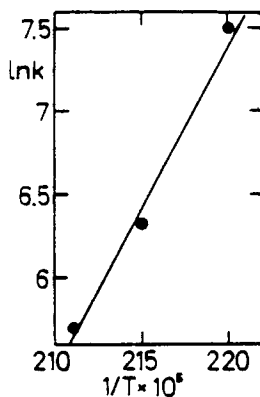


Fig. 6. Rate of thermal crystallization ($\ln k$) of Acala 4-42 cotton vs. $1/T \times 10^5$; $E_{act} = 32.5$ kcal/mol.

Heat Induced Changes in Fine Structure

In Table V and Figures 4, 5, and 6, data obtained on heat-induced changes in accessibility at 180°C, 190°C, and 200°C in Acala 4-42 cotton fibers are presented. It is evident that the accessibility decreases upon heating by first-order kinetics with regard to the initial LOR content. This decrease is accompanied by a significant and systematic decrease in moisture content. The rate constants obtained for the three temperatures and presented in Table VI are in the range of $6\text{--}34 \times 10^{-5}$, i.e., similar to the rate obtained by Hatekeyama et al. for heating amorphous cellulose.⁷

Heat-induced changes in behavior of cellulose have been noticed before by a number of authors. Rushnak and Tanczos also found a decrease in moisture regain and dyeability upon curing celluloses at 190°C and ascribed it to decreased accessibility, but did not study the kinetics.²⁵ Back and co-workers^{26,27} suggested that the increase in crystallinity is caused mainly by crosslinking reactions between aldehyde groups and hydroxyl groups of adjacent chains producing ether linkages. This explains the decrease in moisture content and the increase in the wet tensile strength which they observed. Lewin et al. also postulated the formation of etheric linkages during dehydration in pyrolysis at 250°–275°C. This anhydrization reaction was found to increase in extent with the increase in the LOR content of the cellulose. The reaction proceeded according to a first-order kinetics, and its rate was found to increase with orientation. At 251°C, the rate constant was in the range of $24\text{--}5.6 \times 10^{-2}$ for rayons of 20–60% stretch.^{8,9}

Furthermore, it is also possible that, due to the drying of the cellulose, the

TABLE VI
Rates and Energies of Activation of Crystallization

Polymer	Medium	Temp (°C)	$k \times 10^5$ (s ⁻¹)	Degree of cor	E_{act} (kcal/mol)	Remarks
Cotton	Br ₂ , 0.09	25	3.34	0.99	10.9	Ref. 2
Acala 4-42	mol/L	32	6.50	0.98		
		41	9.07	0.97		
Cotton	Br ₂ , 0.17	25	18.4	0.99		present
Acala SJ-1	mol/L					paper
High mod	Br ₂ , 0.17	25	173		13.1	Ref. 3
rayon	mol/L	32	393			
		40	536			
Bleached	Br ₂ , 0.17	32	0.31	0.87	11.4	present
sulphite pulp	mol/L	40	0.5	0.92		paper
Bleached	Br ₂ , 0.17	25	0.05	0.86		present
sulphate	mol/L	40	0.144	0.93	12.8	paper
pulp	Cl ₂ , 0.1	25	0.16	0.78		
	mol/L					
Cotton	Heating	180	6.51	0.98		present
Acala		190	18.4	0.99	32.5	paper
4-42		200	33.1	0.99		
Amorphous	Heating	94–	1.1–71.7		31–46	Ref. 8
cellulose		150				
PET fibers	Benzene	25–40	1.1–2.7		19.6	Ref. 28
PET film	Heating	96–	13.3–33.0		37	Ref. 29
		119.5				

hydrogen-bonded water molecules are removed, allowing new and close hydrogen bonds to be formed between hydroxyl groups of adjacent chains. A part of these bonds may participate in the crystallization process, provided that they are formed between chains aligned in a parallel way conducive to crystallization. Another part of these hydrogen bonds may, however, be formed at random between entangled chains and hinder chain alignment.

Energy of Activation

It is of interest to note that while the rates of crystallization induced by bromine water vary very widely between the various celluloses, e.g., by 4 orders of magnitude (see Table VI), the energy of activation is in all cases in the range of 10–13 kcal/mol, indicating that the same mechanism is responsible for the reaction. It is assumed that three steps are involved in the crystallization: (a) the diffusion of the bromine molecules into the less ordered regions of the cellulose, (b) formation of the bromine–oxygen bridges involving diffusion and alignment of the chains, and (c) removal of the bromine and formation of the hydrogen bonds involved in the crystallization. The second stage, i.e., diffusion of chain segments, appears to be the rate-determining step rather than the diffusion of the bromine molecules, which is much smaller in volume than the anhydroglucose monomer and also less hindered. Water is present in the system, serves as a plasticizer, and increases the mobility and disentanglement of the chain segments by breaking a part of the hydrogen bonds. The formation of the bromine bridges will in itself help breaking random hydrogen bonds between chain segments by the tension in the bridged chains. The cohesion between the chains will be weakened, and a rotation of chain segments will be facilitated with subsequent alignment.

A similar mechanism appears to operate also in the benzene-induced crystallization of poly(ethylene terephthalate) (PET) fibers for which a similar energy of activation, e.g., 10.6 kcal/mol was found at the temperature range of 25–55°C.²⁸ An Avrami type unplasticized thermal crystallization of amorphous PET, however, yielded an energy of activation of 37 kcal/mol from kinetic experiments at 96–132°C.²⁹ This activation energy is in the range of activation energies found by Hatekeyama et al.⁷ for amorphous cellulose, i.e., 31–46 kcal/mol, and of the activation energy of thermal crystallization of cellulose found in the present study, i.e., 32.5 kcal/mol (see Table VI).

The analogy in the activation energies of the crystallization of two different polymers in the plasticized and unplasticized states lends further support to the assumption that the diffusion of chain segments is generally the rate-determining step in polymer crystallization. It also focusses attention on the similarities in crystallization mechanisms between two widely chemically different polymers. By assuming the activation energy of 32.5 kcal/mol found in the present study to remain constant up to 250°C, a value of the rate constant for the thermal crystallization of cellulose at this temperature of 8.96×10^{-2} was calculated. This value is of the same order of magnitude as 5.56×10^{-2} found for the anhydridization reaction by pyrolysis experiments performed at 250°C on rayon cellulose of 60% stretch.⁸

Thus it appears that the oxygen bridges are responsible to a large extent for the decrease in accessibility in the whole range of 130–250°C. While these etheric

linkages are stable and persist in the structure of heat-treated celluloses, the bromine linkages formed during the crystallization process induced by bromine water are transient and replaced by strong hydrogen bonds formed between adjacent hydroxyl groups. The ketone groups formed on C-2 and C-3 carbons of the anhydroglucose units by oxidation during the bromine treatment may also participate in the formation of strong hydrogen bonds responsible for the crystallization.³⁰

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