Supramolecular Structure of Propionylated Cotton Cellulose

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Synopsis

Heterogeneous propionylation of cotton cellulose, in the form of yarn, was carried out by reaction with propionyl chloride, in a medium of pyridine and dimethylformamide (DMF). The product was a mixed propionate–α-propionylpropionate ester of DS varying from 0.24 to 2.94. The supramolecular structure of these esters was studied by kinetic analysis as well as by the measurements of density, refractive index, and x-ray diffraction. The Sakurada plot of DS against time of reaction showed a discontinuity at a DS of about 2.0, where the x-ray diffraction pattern shows almost complete loss of crystalline structure. The interpretation, based on the assumption that the Sakurada curve actually represents the sum of two simultaneous rate processes acting in the amorphous phase and at the crystalline surfaces, seems to explain the data adequately. The density showed a continuous decrease, consistent with the idea of continuous destruction of crystalline structure with progressive substitution. Refractive indices showed a continuous decrease with substitution and birefringence was almost absent at complete substitution. The calculated value of molar refraction for the sample of DS 2.94 agreed closely with the experimentally observed value. The x-ray diffraction intensity traces gave convincing evidence of the progressive decrystallization of cellulose with the degree of substitution. Decrystallization seems to be more or less complete at about a DS of 2.0.

INTRODUCTION

A considerable amount of research work has been carried out with esters of cellulose, particularly cellulose acetate, whereas the next higher homolog, the propionate, seems to have received relatively little attention. Previous work with this ester was confined to a rather low degree of substitution[1] or was concerned with linters or wood pulp as the starting material.[2] The purpose of the present work was to prepare a series of esters of cellulose with progressive degrees of substitution by reaction of cotton yarn with propionyl chloride and to study their structure and properties. It was found that the product of this reaction, under the conditions stated below, was a mixed ester of cellulose propionate and cellulose propionylpropionate, the latter constituting about one-fourth of the total degree of substitution.[3]

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The changes in the fine structure of these materials with progressive substitution, as indicated by measurements of density, refractive index, x-ray diffraction, and kinetic analysis, are reported in this paper.

EXPERIMENTAL

Materials

Cotton. 7/2 Cotton yarn, commercially mercerized, was used for the preparation of the esters.

Chemicals. Propionyl chloride and N,N-dimethylformamide (DMF) were Eastman reagent grade and were used as such. Pyridine and methanol were Baker analyzed reagent grade.

Apparatus. The reaction was carried out in the reactor described by Stanonis et al.[4] This device keeps the yarn under controlled tension while permitting contraction due to swelling and reaction, thus contributing to uniform and limited shrinkage. This apparatus was modified slightly during the course of the present investigation by the introduction of a glass jacket for circulation of tap water around the exposed circulation tube, thus enabling better control of temperature.

Procedure

The acid chloride–pyridine procedure[2] was chosen as the esterification method for its general applicability for the preparation of cellulose esters of fatty acids, its higher rate of reaction without pretreatment of the cellulose, and its ability to give products with relatively little degradation. The highly exothermic reaction of propionyl chloride with pyridine produces a sticky, yellow solid, soluble in DMF. The reaction with cotton of the reagent so prepared (believed to be an intermediate compound of pyridine and propionyl chloride) is again exothermic and is likely to give rise to side reactions unless diluted with a large amount of another solvent. Malm and co-workers,[2] who carried out the reaction in a homogeneous phase, used a large amount of 1,4-dioxane in order to avoid side reactions and to keep the products in solution. In the present case, the reaction was intended to be carried out in a heterogeneous phase and DMF was used as a diluent. The use of DMF is advantageous in that it keeps the intermediate compound in solution at the temperature of the reaction (75°C.), does not dissolve the resulting ester, diminishes the temperature rise due to the heat of reaction by dilution to a larger volume, and reduces the viscosity of the medium, thus facilitating circulation of the reagents in the reactor.[4] McKelvey et al.[5] have reported that DMF is an almost ideal medium for cellulose esterification reactions because of its capacity for hydrogen-bond breaking, its action as an ionizing medium because of high dielectric constant, its aprotic nature, and its ability to complex with Lewis acids.

It was found in preliminary runs that it was necessary to have a large excess of propionyl chloride (four times the calculated equivalent of hydroxyl groups in the cellulose) in order to approach full substitution. The molar ratio of pyridine to acid chloride was 2:1, which was more than sufficient to neutralize all the hydrochloric acid produced in the reaction. The remainder of the volume was made up with DMF, the reactor requiring about 700 ml. total for efficient operation and for submerging the cotton spool. In a typical run, 20 g. of cotton yarn was reacted with 120 ml. of propionyl chloride in 240 ml. of pyridine and 340 ml. of DMF.

The required amount of propionyl chloride was added dropwise with stirring to a mixture of measured volumes of pyridine and DMF at 5–10°C. A white precipitate formed, which turned yellow and then red, the color deepening as more acid chloride was added. On heating to 35–40°C. the precipitate dissolved, forming a brown solution. The solution was heated to the temperature of the reaction (75°C.) and added to the dried, preheated sample of yarn, wound on the Teflon cylinder,[4] and kept inside the reactor at the bath temperature of 75°C. Due to the exothermic nature of the reaction, the temperature of the reacting liquid tends to increase for the first few minutes but could be kept within ±5°C. by circulation of cooling water in the jacket of the reactor. After this, a small amount of cooling water sufficed to keep the temperature constant within ±2°C. Contraction of the Teflon cylinder, as a result of swelling of the cellulose, was more rapid at the beginning of the reaction and was roughly proportional to the progress of the reaction. The reaction was continued for different periods, up to a maximum of 5 hr., depending on the degree of substitution desired.

When the yarn is held in a tightly wrapped condition on the spool, the reaction falls far short of full substitution, even when the reaction time is prolonged. More complete substitution was achieved in the case of the two samples of DS 2.34 and 2.94 by conducting the reaction in two steps. In the first step the reaction was stopped after 1–2 hr., depending on the substitution desired. The sample was then washed, dried, and rewrapped inside out, so that all portions would have equal exposure to the fresh reactants when reacted again.

Samples

The degrees of substitution (DS) of the samples included in this study, as measured by saponification,[6] are as follows: 0.24, 0.37, 0.44, 0.75, 1.01, 1.37, 1.72, 2.00, 2.34, and 2.94. The propionylpropionate moiety which arises out of secondary reaction of the propionate already formed was found to be about one-fourth of the total at all degrees of substitution.[3] A control sample was prepared by using all the reagents except propionyl chloride and treating in an identical manner.

The samples were colored white to pale yellow, the color deepening with substitution.

A peculiarity, observed with the completely esterified sample (DS 2.94), is its insolubility in solvents which are reported to dissolve tripropionates.[7] The difference may be attributed either to the pendant α-propionylpropionyl group resulting under the present reaction conditions which might decrease the solubility of the ester, or to the higher degree of polymerization of the cotton fiber compared to the regenerated cellulose which was used by Malm and co-workers as the starting material, or both.

Details of the experimental conditions for preparation of the different samples and their degree of substitution by weight and by saponification are summarized in Table I. The reason for the higher degree of substitution by weight than by saponification has already been suggested.[3]

Test Methods

Density. Density was determined in an anhydrous n-heptane–carbon tetrachloride column, following the method as outlined by Conrad et al.[8] The computed densities were averaged. The range of particle displacement in the stratified layer provided a measure of the uniformity of substitution.

Refractive Index. Refractive indices of the fibers were measured as described by Tripp et al.[9]
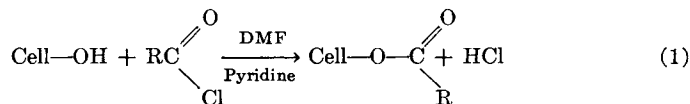
X-Ray Diffraction. The x-ray diffractograms were prepared as described by Conrad and Creely,[10] except that instead of using recorder tracings, the number of seconds required for 1000 counts was determined for each 0.25° over the 2θ range 5–30° and the reciprocal used as a measure of intensity. The precision in terms of standard deviation at any point on the curve was about 3%.

Color Test for Uniformity. The uniformity of substitution was determined with a dye test,[11] Heliotrope B being used as a cotton color and Celliton Fast Yellow to color the substituted product. These results had a direct correlation with the degree of substitution.

RESULTS AND DISCUSSION

Kinetic Analysis

Cellulose esterification may essentially be represented by relation (1):

$$\text{Cell}-\text{OH} + \text{RC} \overset{O}{\underset{Cl}{\diagdown}} \xrightarrow[\text{Pyridine}]{\text{DMF}} \text{Cell}-\text{O}-\text{C} \overset{O}{\underset{R}{\diagdown}} + \text{HCl} \tag{1}$$

However, in actual practice the reaction is much more complicated. Not only is the reaction taking place in a heterogeneous phase, between a liquid and a solid substance, but in addition the solid consists of two phases, crystalline and amorphous cellulose, which are present in a submicroscopically mixed form, though in a continuous structure. Also, the reagent, propionyl chloride, probably forms a complex with pyridine and/or DMF before reacting with the solid substrate.

TABLE I
Summary of Samples

Sample no.	Weight of cotton taken (air-dried), g.	Nature of wrapping	Equivalents of			Time, min.	Temp., °C.	Degree of substitution	
			Cell. OH	Prop. chloride	Prop. anhydride			By wt.	By saponification
1	40	Tight	1	2	—	75	75	1.35	1.01
2	40	"	1	2	—	300	75	1.67	1.17
3	40	"	1	2	—	300	100	0.90	0.58
4	20	Loose	1	4	—	15	75	0.33	0.24
5	20	"	1	4	—	20	75	0.63	0.37
6	20	"	1	4	—	30	75	0.73	0.44
7	20	"	1	4	—	45	75	1.12	0.75
8	20	"	1	4	—	75	75	1.71	1.37
9	20	"	1	4	—	100	75	2.52	1.72
10	20	"	1	4	—	180	75	2.88	2.00
11[a]	20	"	1	4	—	90 + 90[a]	75	3.40	2.34
12[a]	20	"	1	4	—	120 + 120[a]	75	4.27	2.94
13[a]	20	"	1	4	—	60 + 7[a]	75	2.10	1.54
14	20	"	3	4	8	180	75	0.70	0.69
15	20	"	3	4	8	360	75	0.90	0.85

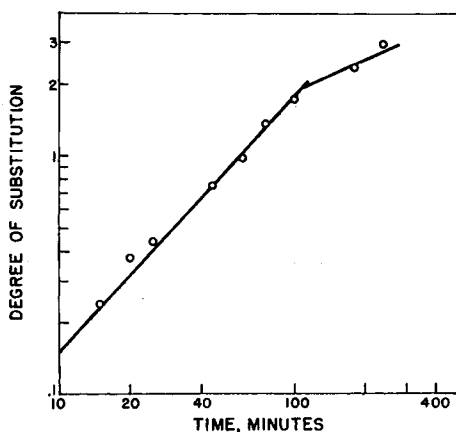[a] Prepared by two-step method.

Fig. 1. Sakurada plot of the propionylated samples.

Sakurada,[12] as a result of investigations on the heterogeneous rates of reaction of cellulose with various substances, enunciated the idea of a "diffusion-controlled kinetics" and proposed that the rate is governed by the equation,

$$S = Kt^m \qquad (2)$$

where S is degree of substitution, t is time of reaction, and K and m are constants. Thus, when the logarithm of the amount of substitution S is plotted against the logarithm of the time of reaction, a straight line should be obtained. Sakurada and co-workers[13,14] showed that this was generally obeyed. Some of their data indicated the presence of two intersecting straight lines, but Sakurada interpreted the second as being due to the termination of reaction, with slope equal to zero. Conrad et al.,[8] in studies of acetylation of cellulose, also found two intersecting straight lines, the point of intersection being at about DS = 1.95. Conrad et al. in their studies on kinetics of cyanoethylation,[15] propionylation,[16] and benzoylation[17] of cellulose faced a similar situation and came to the conclusion that the first steep portion of the Sakurada curve is actually the sum of two simultaneous rate processes: (a) all the noncrystalline portions of the cellulose are immediately accessible to a diffusion-controlled process; (b) new accessible cellulose is continuously produced at a kinetic rate by reaction at the crystallite surfaces. The effect of the latter process is to augment continuously the amount of cellulose hydroxyls available for the reaction. During the last stage, when the crystalline cellulose has become exhausted and only the residual accessible noncrystalline cellulose undergoes reaction, the rate is noticeably decreased. This occurs at about DS = 2, as shown in Figure 1. This mechanism of cellulose reaction is supported by the x-ray diffractograms (Fig. 4, below) which indicate almost complete destruction of the crystalline phase at this level of substitution.

Density

When the densities of the samples were plotted against the degree of substitution they fell at the points indicated by circles in Figure 2. The density is curvilinear with substitution. A least-square line fitted to the observed densities d yielded the following hyperbolic equation:

$$d = 1.279 + 0.196/(DS + 0.779) \qquad (3)$$

This equation is plotted as a smooth line through the observed points in Figure 2.

Equation (3) gives a limiting density of 1.331 g./cc. at maximum degree of substitution. This value is very near to the published density for triacetates, 1.346 (Conrad et al.[8]), 1.326 (Orr et al.[18]), and 1.351 g./cc. (Sprague et al.[19]). On the other hand, the values for density are consistently higher at all degrees of substitution than those reported for propionates by Malm et al.[20] and the value for the completely substituted material (1.331 g./cc.) is much higher than that for the tripropionate (1.21 g./cc.) as reported by these workers. The density of the unmodified cotton fiber was 1.531 g./cc. in comparison with values of 1.550 found by both Conrad[8] and Orr.[18] This difference is due to the difference in the starting material, the sample of Conrad et al.[8] consisting of native cellulose,
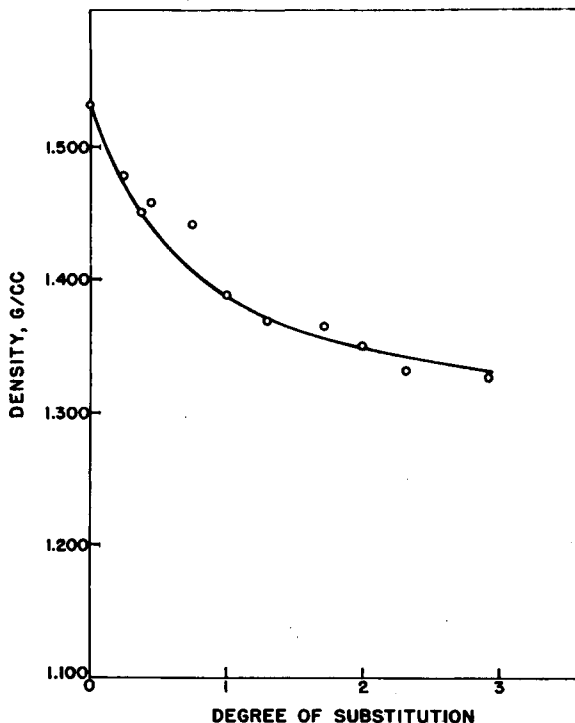

Fig. 2. Least-square fit of density vs. degree of substitution.

whereas the mercerized cellulose used in the present study is known to have a distinctly lower density.[21] The per cent decrease of density for the same degree of substitution is greater in the present case than that of Conrad et al.,[8] due to acetylation. This is due primarily to the more bulky side chains of propionylpropionate which do not fit well into the noncrystalline substance.

The density of dry cellulose in a nonswelling liquid depends on the percentage of crystalline material, the crystalline form and the state of the amorphous portion. Since the density of the crystalline portion is higher than that of the amorphous portion,[21] the gradual conversion of the crystalline part to the amorphous structure is expected to result in a corresponding decrease of density which is reflected in Figure 2. This decrease of density fits in with the idea of gradual destruction of the crystalline structure with increase of substitution.

Refractive Index

The study of the changes of refractive index that accompany chemical modification of cotton has received considerable attention in the past. Tripp et al.[9] observed that the optical anisotropy of cotton disappears progressively and completely and even reverses sign as acetylation proceeds to completion. Loss of anisotropy strongly suggests loss of orientation due probably to the destruction of crystal structure on substitution, as well as to change in polarizability of the cellulose ester moiety.

The results of the measurements of refractive indices for the samples under study are portrayed in Figure 3. The average refractive index of cotton, as measured in unpolarized light, shows a continuous decrease as substitution increases. The same holds good for the indices measured with light vibrating parallel $(n_{\|})$ and perpendicular $(n_{\perp})$ to the fiber axis. The average index, calculated as arithmetic mean, was nearer to the experimental value than that calculated by the method of Hermans.[21] The curves obtained from the values of refractive indices all approach a common value at the point of maximum substitution (DS = 2.94) where birefringence $(n_{\|} - n_{\perp})$ is essentially zero. The completely substituted material had uniform polarizability in all directions due probably to the production of a more random amorphous structure and to the presence of the ester side groups. At other points, birefringence shows a somewhat irregular behavior though showing the trend of decreasing birefringence with increasing DS. The reason for this, revealed by the dye test,[11] was traced to the microscopic non-uniformity of substitution in the sample.

Considering that the esters prepared in the present investigation have three-fourths of the cellulose hydroxyls reacted as propionate and one-fourth as α-propionylpropionate,[3] the calculated molar refraction based on the Lorentz-Lorenz formula[22] for a completely substituted material would be 76.3. This may be compared to 67.7 computed for the tripropionate and 102.1 for the tripropionylpropionate. The observed molar refraction R
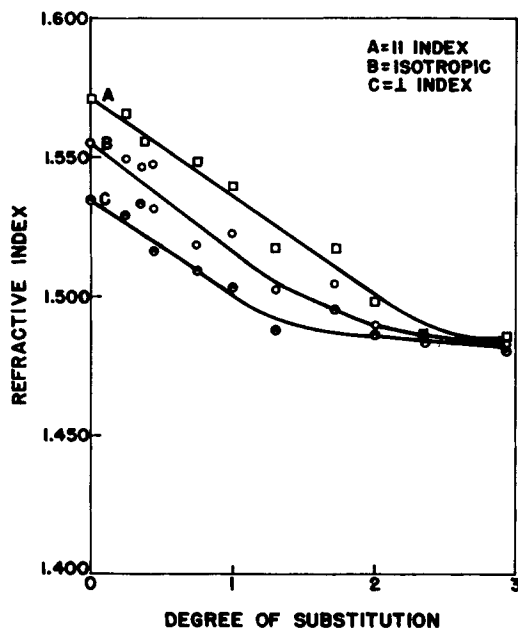
Fig. 3. Variation of refractive indices with degrees of substitution.

obtained from the Lorentz-Lorenz equation for the sample of DS 2.94, taking it to be completely substituted, was 79.9, which is in good agreement with the above considering the precision of the measurements involved. The good agreement between the theoretical and the observed molar refraction lends support to the composition of the ester as proposed in the earlier communication.[3]

X-Ray Diffraction

The x-ray diffraction intensity traces of the various samples are shown in Figure 4. The control sample (DS = 0), shows both cellulose I and cellulose II peaks characteristic of the partially mercerized material. Decrystallization of the samples with progress of substitution is evident by the decrease of the strong (002) cellulose interferences at $2\theta \approx 22°$, this being displaced to 22.25° due to the overlapping interference of the cellulose II peak. Decrystallization starts even at DS = 0.24 and is virtually complete at about DS 2.0.[16] The two samples having DS higher than 2 show essentially the same amorphous pattern in which the original (002), (101), and (10$\bar{1}$) peaks at $2\theta \approx 22$, 14.8, and 16.6°, respectively, have practically disappeared. Simultaneously with the loss of these peaks, a new diffuse diffraction halo appears at about $2\theta = 7.5°$ which begins to develop even at a DS of 0.24. The results are consistent with similar studies with cellulose acetate.[10] However, no crystallization could be induced on heating the sample, as was observed in the studies of Conrad and Creely[10] with the
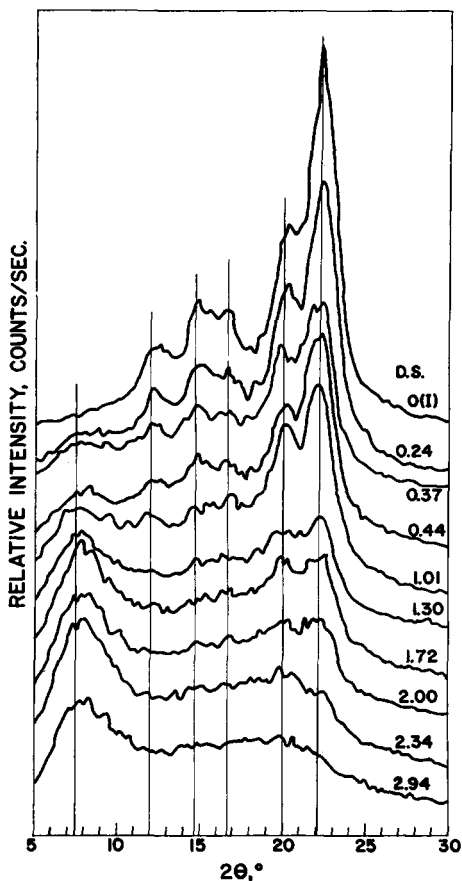
Fig. 4. X-ray diffraction profiles of propionylated yarns.

corresponding acetates.   The difference may be attributed to the simultaneous presence and bulkiness of the α-propionylpropionate, which destroys the symmetry of the structure and thus prevents crystallization.

The progressive decrystallization of the cellulose structure is also evident when the ratios of the maxima of the diffractograms at $2\theta = 22.25°$ to the minima at $2\theta = 18°$ are plotted against DS (Fig. 5) as was done by Conrad and Creely.[9]   This shows a linear relationship up to DS of 2.34 in spite of the error due to overlapping interferences of the cellulose II (002) peak.

CONCLUSIONS

Propionylation of cotton cellulose with propionyl chloride in a medium of pyridine and DMF proceeds heterogeneously, up to essentially complete substitution by what appears to be a diffusion-controlled reaction.
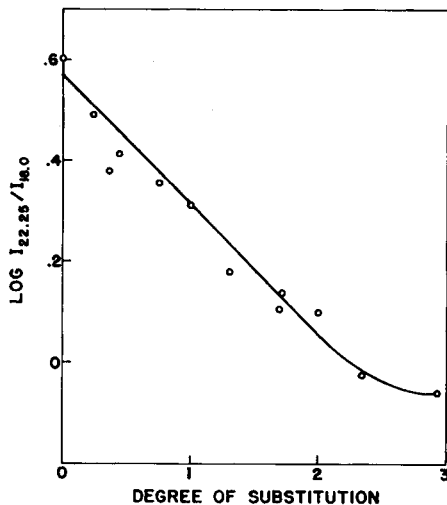
Fig. 5. Relation of relative intensity of the 002 interference to degree of substitution.

The progressive loss of crystalline structure with almost complete disruption at DS = 2.0 and above as propionylation proceeds, is reflected in kinetic analysis, density and refractive index measurements and is confirmed by x-ray diffraction intensity patterns.

The presence of the bulky propionylpropionate side chains destroys the symmetry of the structure, and no crystallization could be induced on heating the substituted material.

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Résumé

La propionylation hétérogène de la cellulose de coton, sous forme de film a été effectuée par réaction du chlorure de propionyle dans un milieu pyridine et dimethylformamide (DMF). Le produit était un ester mixte propionique–α-propionylpropionique de DS variant de 0.24 à 2.94. La structure supramoléculaire de ces esters a été étudiée par analyse cinétique aussi bien que par des mesures de densité, d'indice de réfraction et de diffraction aux rayons-X. Le diagramme de Sakurada de DS en fonction du temps de réaction montrait une discontinuité à un DS d'environ 2.0, lorsque le réseau de diffraction aux rayons-X montrait pratiquement une perte complète de la structure cristalline. L'interprétation basée sur l'hypothèse que la courbe de Sakurada représente réellement la somme de deux processus de vitesse simultanément, agaissant sur la phase amorphe et aux surfaces des cristallites, semblait expliquer adéquatement les résultats. La densité montrait une diminution continuelle, consistant avec l'idée d'une destruction continue de la structure cristalline avec la substitution progressive.

Zusammenfassung

Die heterogene Propionylierung von Baumwollcellulose in Form von Garn wurde durch Reaktion mit Propionylchlorid in einem Pyridin-Dimethylformamid (DMF) -Medium durchgeführt. Als Produkt wurde ein gemischter Propionat–α-Propionylpropionat-Ester mit DS von 0,24–2,94 erhalten. Die übermolekulare Struktur dieser Ester wurde mittels einer kinetischen Analyse und durch Dichte-, Brechungsindex und Röntgen-beugungsmessungen untersucht. Das Sakurada-Diagramm von DS gegen die Reaktions-dauer zeigte eine Diskontinuität bei einem DS von etwa 2,0, wo das Röntgendiagramm einen fast völligen Verlust der Kristallstruktur anzeigt. Eine Interpretation auf Grund-lage der Annahme, dass die Sakurada-Kurve tatsächlich die Summe der Geschwindig-keit zweier simultaner, in der amorphen Phase und an den Kristallitoberflächen statt-findenden Prozesse darstellt, scheint die Daten befriedigend erklären zu können. Die Dichte zeigte eine kontinuierliche, mit der Vorstellung einer kontinuierlichen Zerstörung der kristallinen Struktur bei fortschreitender Substitution vereinbare Abnahme.