Preparation of Higher Aliphatic Acid Esters of Wood in an N_2O_4–DMF Cellulose Solvent Medium*

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Synopsis

Esterification of wood meal with a series of aliphatic acid anhydrides and acid chlorides in a nonaqueous cellulose solvent, an N_2O_4–DMF solvent, has been studied. The N_2O_4–DMF–pyridine solution used as the reaction medium plays a role in destroying the molecular order of the cellulose within the wood, enabling the cellulose to be uniformly substituted by acyl groups along its chain. These uniformly distributed blocking groups result in the permanent decrystallization of the wood. The acyl blocking groups are best achieved by esterification using acid chlorides in the nonaqueous solvent. Acid chlorides, from caproyl to stearoyl chloride, were found to be much more effective as acylating agents than acid anhydrides, from propionic to caproic anhydride. Although no difference in reactivity can be recognized among the acid chlorides, the reactivity decreases with increase in the number of carbon atoms in the acyl group among the acid anhydrides.

INTRODUCTION

During the last ten years, several nonaqueous cellulose solvents have been found[1] and their nonaqueous nature has enabled homogeneous reactions of cellulose utilizing organic reagents.[2-9]

On the other hand, we found that even if wood meal was treated with the nonaqueous cellulose solvents under conditions suitable for dissolving isolated cellulose, the cellulose component was not extracted from the wood cell wall.[10-12] Based on this finding, specific decrystallization methods for wood have been developed.[11,12] In this connection, acetylation of wood in nonaqueous cellulose solvents has been studied.[8,12] The introduction of the acetyl group by this method was found to result in the fairly permanent decrystallization of wood.

Based on our previous work,[12] we report the preparation of a series of esters, from the propionate to the stearate within wood structure, using a dimethylformamide (DMF) solution of dinitrogen tetroxide (N_2O_4) as the reaction medium.

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EXPERIMENTAL

Samples and Reagents

Wood meal (48–60 mesh) from the sapwood of Makanba (*Betula maximow-icziana* Regel) was used after extracting and washing with cold water. Partially acetylated wood (acetyl content 4.8–23.4%) used in a part of this study was prepared by the acetic anhydride–pyridine procedure. DMF, the principal component of the cellulose solvent, was analytical reagent grade, and N_2O_4 supplied in a cylinder (Seitetsu Kagaku Co.) was used after blowing it through a flask and liquifying it by cooling. Analytical reagent-grade pyridine, acid anhydrides from propionic to caproic anhydride, and acid chlorides from caproyl to stearoyl chloride were used as acylating agents.

Esterification of Wood with Acid Anhydrides in an N_2O_4–DMF–Pyridine Medium

Wood meal (1.3 g) was dried overnight *in vacuo* at 105°C, weighed, and placed in a 200-ml ground-glass stoppered Erlenmeyer flask. After redrying, DMF (25 ml) was added, and then N_2O_4 (6 moles per mole glucose unit of cellulose) was injected with the aid of a syringe. The amount of N_2O_4 added was based on the assumption that the content of cellulose in wood is 50%. The reaction vessel was stoppered and allowed to stand for 24 hr at 25°C in order to ensure that the wood sample was completely decrystallized. Then, to this reaction mixture pyridine (25 ml) and the appropriate aliphatic anhydride (50 ml) were successively added. Subsequently, the reaction was continued for a definite period at 25°C. After the reaction, the aliphatic acid esters of wood were collected by filtration and washed with deionized water. The products were further purified by (1) extraction with deionized water for 24 hr, (2) extraction with ethanol for 12 hr, (3) exposure to steam for 30 min, and (4) washing with distilled water. Finally, they were dried in air at room temperature and *in vacuo* at 70°C.

Esterification of Wood with Acid Chlorides in an N_2O_4–DMF–Pyridine Medium

DMF (25 ml) was added to weighed and redried wood meal (1.3 g) and then N_2O_4 (6 moles per mole glucose unit of cellulose) was injected. After the mixture was allowed to stand for 24 hr at 25°C, pyridine (25 ml) and the appropriate amount of the acid chloride were successively added dropwise through a pressure compensated dropping funnel with continuous stirring and cooling. Subsequently, the reaction was continued for a definite period at 25°C. After the reaction period, the reaction mixture was poured into an excess of a water–methanol solution (1:2). The acylated wood meal was filtered, washed with water–ethanol, and dispersed again in an excess of fresh water–ethanol (1:2). It was allowed to stand for at least 12 hr with mild stirring. Subsequently, the acylated wood meal was extracted with ethanol in a Soxhlet extractor for over 48 hr and was again washed with distilled water. The sample was then dried first in air and finally *in vacuo* at 70°C.

Esterification of Wood with Acid Chlorides in a DMF–Pyridine Medium

The esterification of wood in DMF–pyridine was carried out using a similar procedure, except that N_2O_4 was not utilized as a component of the reaction medium.

Acyl Contents

The acyl contents of a series of acylated wood samples, from propionate to caproate, were determined by an established saponification method.[13] However, the values are expressed as the amount of acyl group per remaining wood substance. The acyl content of those from caproate to stearate were determined by a gravimetric method. Figure 1 shows the relationship between the ester content obtained for caproylated wood by the saponification method and the corresponding value of weight increase (W.I.) determined by the gravimetric method. A fairly good linear relationship exists between the experimental values.

Infrared and X-Ray Analysis

Infrared absorption spectra were obtained with a Hitachi EPI-G3 grating double-beam infrared spectrophotometer using the KBr disk technique. The absorbance was measured using the baseline technique.

X-Ray diffractograms were obtained with disks of 0.2 g in weight and 1.3 cm in diameter, prepared by compressing acylated wood meal at a pressure of 2.03 ton/cm^2. The equatorial diffraction pattern was measured from 5–35° values of 2θ using Ni-filtered CuKα radiation at 35 kV and 25 mA. Angle 2θ was standardized against an aluminum plate. The equipment used was a Rigaku Denki x-ray diffraction unit Geigerflex 2011B. The operating conditions of the x-ray diffractometry were the same as those described in the previous report.[12]
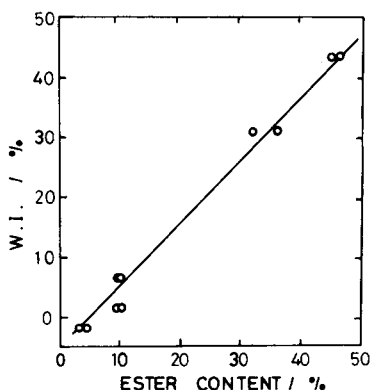

Fig. 1. Relationship between ester content obtained by saponification method and corresponding value of weight increase gravimetrically determined. A series of caproylated wood samples were used for examination.

RESULTS AND DISCUSSION

Function of N_2O_4–DMF–Pyridine System as the Reaction Medium

Cellulose, including the form existing within wood, is partly crystalline. The accessibility of the cellulose to reagents is a major consideration in the esterification of wood. In this connection, a study was made to determine how the N_2O_4–DMF–pyridine solution acts as a reaction medium. It was of interest to determine whether merely intramicellar swelling occurred or whether local dissolution of cellulose within the continuous network of lignin took place from the beginning of the esterification of wood.

In order to elucidate this, a series of acetylated wood samples in which the distribution of the acetyl group was limited to the amorphous region was treated with the N_2O_4–DMF–pyridine solution. The change in the molecular order of cellulose during the treatment followed by recrystallization was investigated by x-ray analysis. The results are summarized in Figure 2. From this figure, it can be seen that even the acetylated wood with the lowest acetyl content (4.8%) shows an almost completely decrystallized x-ray profile after the treatment with the N_2O_4–DMF–pyridine solution and recrystallization, while unacetylated wood (control sample) reveals the cellulose I structure after the same treatment. However, both samples show a similar x-ray diffractogram before the N_2O_4–DMF–pyridine treatment, illustrating that acetylation as small as 5% within the amorphous region of wood has a negligible effect on the equatorial x-ray diffractogram.

These results imply that the N_2O_4–DMF–pyridine reaction medium causes the complete destruction of the molecular order of cellulose within wood and that the acetyl groups introduced initially in the amorphous phase hinder recrystallization after the N_2O_4–DMF–pyridine treatment. In other words, it can be stated that the parts of the cellulose chains which are included within the ordered region at the time of the recrystallization are not limited to those originally having been included in the crystalline parts of natural cellulose within the wood.,
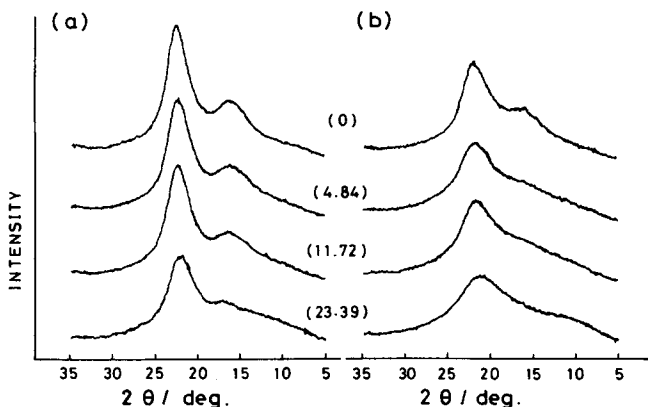

Fig. 2. Comparison of x-ray diffractograms of ununiformly acetylated wood samples (a) before and (b) after the treatment with an N_2O_4–DMF–pyridine solution followed by recrystallization. Numerical values in parentheses represent the acetyl content (g/100 g wood). Wood samples (1.3 g) were treated with cellulose solvent consisting of N_2O_4 (6 moles/mole glucose unit), DMF (25 ml), and pyridine (25 ml) for 24 hr at 25°C. Recrystallization was accomplished by boiling in water and drying at 100°C. All diffractograms were taken with dry samples.

Further, it is interesting to note that, as described above, the x-ray curve for unacetylated wood is not that of cellulose II but that of cellulose I, even after such a strong disordering treatment as local dissolution. It is noteworthy that no conversion of native cellulose I into cellulose II has been known to occur even as a result of strong alkali treatment (mercerization) in the cell wall of wood.[14] The details of this phenomenon will be reported later.

Esterification of Wood with Acid Anhydrides using N_2O_4–DMF–Pyridine System as the Reaction Medium

Representative rate curves for esterification of wood with acid anhydrides in an N_2O_4–DMF–pyridine medium are shown in Figures 3 and 4. In Figure 3, the ester content, expressed as the percentage of acyl group per remaining wood substance and being equivalent to the value of the weight increase of the wood, is plotted on the ordinate. Also in Figures 3 and 4 the molality of the acyl substituent, which is defined as the moles of acyl substituent per 1000 g wood (similar to the molal concentration for solutions) is plotted on the ordinate. The molality of the acyl substituent was adopted for convenience when comparing various kinds of esterified wood.

All of these log–log plots for the esterification process give straight lines,
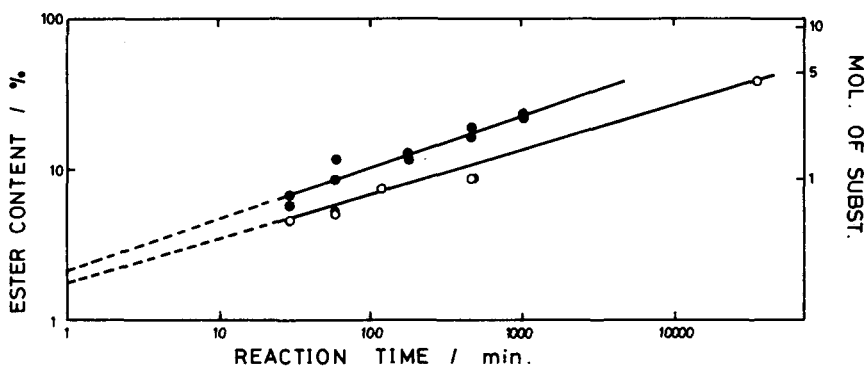
Fig. 3. Rates of butyrylation of wood with n- and isobutyric anhydride in N_2O_4–DMF–pyridine medium.
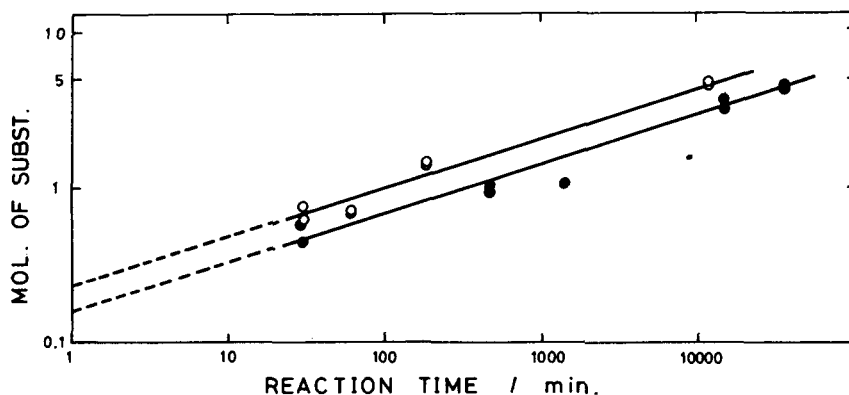
Fig. 4. Rates of valerylation and caproylation of wood with valeric and caproic anhydride in N_2O_4–DMF–pyridine medium.

showing superficially that the rate of the reaction is governed by the diffusion rate of the acylating agent.[15,12] Even though cellulose loses its natural, ordered arrangement of molecules within the cell wall and some homogeneous reaction along the cellulose chain becomes possible by virtue of the action of the N_2O_4–DMF–pyridine medium, the insoluble character of lignin in the reaction medium keeps the state of the wood sample solid and makes the esterification a diffusion-controlled reaction. However, it should be noted that according to Conrad et al.[16] this kind of log–log plot for heterogeneous reactions of cellulose gives two intersecting straight lines, and the point of intersection is associated with the complete decrystallization of the cellulose I structure.

Fundamentally, cellulose exists as a crystalline and a noncrystalline phase. Chemical reactions taking place in the amorphous regions proceed at two independent rates: the rate of diffusion and the rate of the chemical reaction. The chemical reagent cannot diffuse into the crystalline region. It must first react at the chain ends or the surface of the crystallites. This results in the opening of some of the hydrogen-bonded cellulose chains, thus producing some amorphous cellulose. The reagent then diffuses into this newly produced amorphous portion reacting with the cellulose and simultaneously generating more amorphous cellulose. The phenomenon is therefore complex, and the kinetics cannot be treated either as a simple chemical process or as a simple diffusion process. Both processes are occurring concurrently and are dependent on each other.

If our previous results obtained for the acetylation of wood in the same reaction medium (Fig. 9 in our previous report[12]) are taken into account together with the results of Figures 3 and 4, it becomes clear that the reactivity of these acid anhydrides in the esterification decreases with increase in the number of carbon atoms in the acyl group, at least among the normal series. Also from Figure 3 it can be noted that the reactivity of isobutyric anhydride is smaller than that of n-butyric anhydride. At the same time it should be pointed out that the reactivity of these acid anhydrides toward cellulose is not large. The molality of the acyl substituent is expected to have a maximum value of 18.5 and approximately 13 for acylated cellulose and acylated wood, respectively, whereas the obtained values are 6.08 for propionylated wood after 591 hr of reaction, 3.23 for n-butyrylated wood after 18 hr of reaction, 5.40 for isobutyrylated wood after 591 hr of reaction, 4.80 for valerylated wood after 193 hr of reaction, and 4.64 for caproylated wood after 591 hr of reaction.

However, compared with the recent attempts of Russo et al.,[17] who failed to acetylate dissolved cellulose in N_2O_4–DMF using a variety of reagents, it can be said that our results for a similar reaction are favorable and the preparation of even higher homologs of cellulose acetate becomes possible, although the degrees of substitution obtained are small and a longer reaction period is required.

The acylation of wood with acid anhydrides in an N_2O_4–DMF–pyridine medium results in the structural characteristics represented in Figures 5(a) and 5(b). It was shown previously that the aceylation of wood in a DMF–pyridine medium resulted in the acetylated wood having an apparent but decrystallized cellulose I pattern even at acetyl contents of 23.4%,[18] whereas the same reaction in an N_2O_4–DMF–pyridine medium resulted in almost perfectly decrystallized wood within the reaction time of 10 min, with acetyl contents of 6.0%. It can be seen from Figure 5 that the reaction times required for obtaining almost perfectly decrystallized wood are at least 1 hr and 24 hr for propionylated wood and ca-
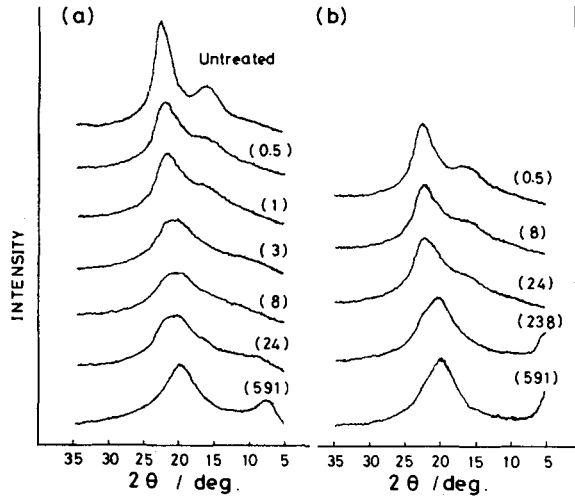
Fig. 5. X-Ray diffraction curves of wood propionylated (a) and caproylated (b) with the corresponding acid anhydrides in an N_2O_4–DMF–pyridine medium. Numerical values in parentheses represent reaction time (hr).

proylated wood, respectively. Taken together, these results indicate that, in order to permanently decrystallize wood by this procedure, it is necessary to employ longer reaction times as the molecular weights of the anhydrides increase, to compensate for their lower reactivity.

Esterification of Wood with Acid Chlorides using an N_2O_4–DMF–Pyridine Solution as Reaction Medium

Effect of Changes in Reaction Variables in the Procedure for Lauroylation at 25°C

The effect of the concentration of the acid chloride on the esterification is shown in Figure 6. At first, the degree of esterification increases with increase in the amount of lauroyl chloride, but it levels off around 50 ml. Corre-
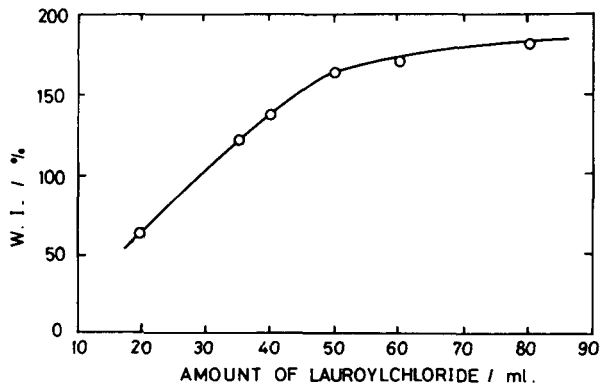

Fig. 6. Influence of amount of lauroyl chloride on degree of lauroylation of wood in N_2O_4–DMF–pyridine medium. Reaction conditions: wood meal, 1.3 g; N_2O_4, 6 moles per mole glucose unit; DMF, 25 ml; pyridine, 25 ml; reaction temp., 25°C; reaction time, 20 hr.

spondingly, in the related x-ray diffractograms the degree of superimposition of a cellulose laurate pattern on that characteristic of a distorted cellulose I lattice and the degree of decrystallization of the modified wood increase with the amount of the acid chloride until it reaches 50 ml.

The effect of the amount of pyridine is illustrated in Figure 7. It is known that an increase in the amount of pyridine beyond 20 ml results in a decrease in the degree of esterification, but the change between 20 and 30 ml is very small. On the other hand, the reaction is suppressed without pyridine.

The relationship between the amount of DMF and the degree of esterification, shown in Figure 8, indicates that the optimum amount of DMF is between 25 and 60 ml. Although the amount of DMF does not appreciably affect the degree of esterification, its existence as a component of the reaction medium prevents the entire solution from solidifying by the formation of a large amount of brown-colored crystals when the acid chloride is added. In addition, it is found from the x-ray diffractograms that fairly advanced decrystallization and an appreciable superimposition of the cellulose laurate pattern are obtained equally for all the lauroylated wood samples concerned. This suggests that uniform and
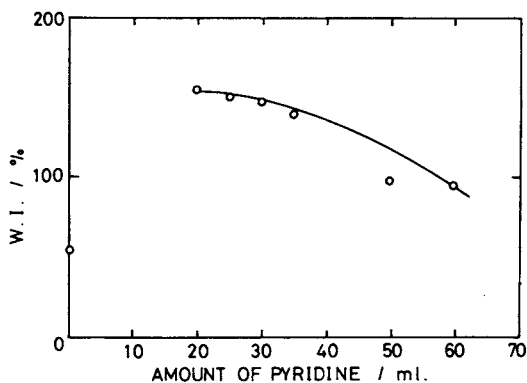

Fig. 7. Influence of amount of pyridine on degree of lauroylation of wood in N_2O_4–DMF–pyridine medium. Reaction conditions: wood meal, 1.3 g; N_2O_4, 6 moles per mole glucose unit; DMF, 25 ml; lauroyl chloride, 50 ml; reaction temp., 25°C; reaction time, 20 hr.
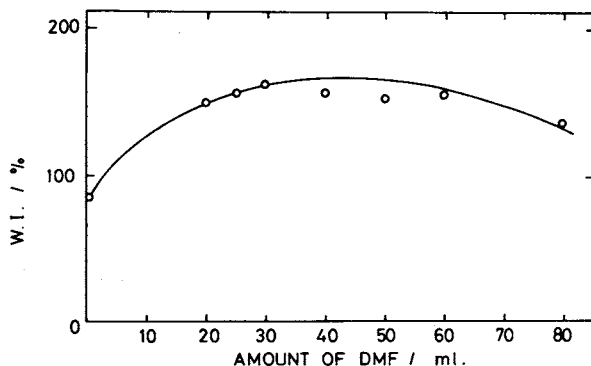

Fig. 8. Influence of amount of DMF on degree of lauroylation of wood in N_2O_4–DMF–pyridine medium. Reaction condition: wood meal, 1.3 g; N_2O_4, 6 moles per mole glucose unit; pyridine, 30 ml; lauroyl chloride, 50 ml; reaction temp., 25°C; reaction time, 20 hr.

advanced esterification along the cellulose chains takes place within wood, regardless of the amount of DMF.

From the above experiments, a reaction system with 1.3 g wood meal, 6 moles per mole glucose unit of N_2O_4, 25 ml pyridine, 25 ml DMF, and 50 ml lauroyl chloride can be chosen tentatively as a standard. Under these conditions, lauroylated wood with a substituent molality of 9.29 was obtained after 20 hr at 25°C. By comparison with the corresponding values obtained previously for the esterification with acid anhydrides, it can be said that acid chlorides are much more effective as acylating agents.

This fact is also evident from a simple comparison of the infrared spectra in Figure 9. The degree of esterification attained in 591 hr with acid anhydrides is almost equal to that attained in 1 hr with lauroyl chloride. On the other hand, in Figure 9(a) the spectrum for the longest reaction period (48 hr), in which the band for the O–H stretching vibration becomes very weak, was obtained with lauroylated wood having a substituent molality of 10.7. Therefore, the foregoing estimation that the maximum value of the substituent molality for wood is approximately 13 is reasonable.
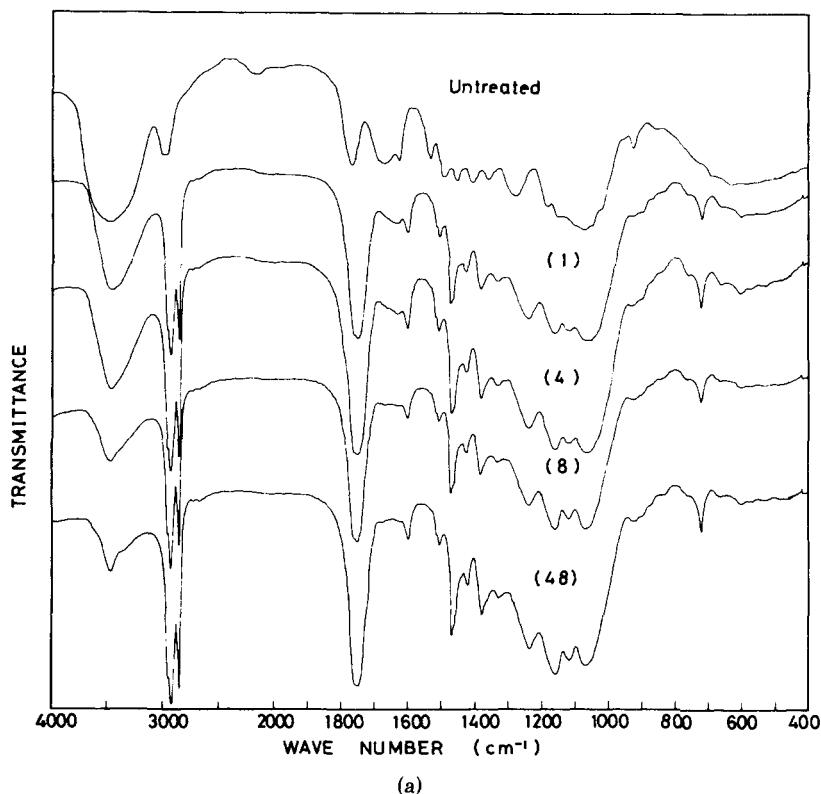

(a)

Fig. 9. Infrared absorption spectra of (a) lauroylated wood prepared by reaction of wood with lauroyl chloride in N_2O_4–DMF–pyridine medium, and (b) a series of esterified wood from propionate to caproate prepared by reaction of wood with corresponding acid anhydride in N_2O_4–DMF–pyridine medium. Numerical values in parentheses in (a) are reaction time (hr). Reaction time for preparing the samples shown in (b) was 591 hr, except that valerylated wood was obtained after 193 hr of reaction.
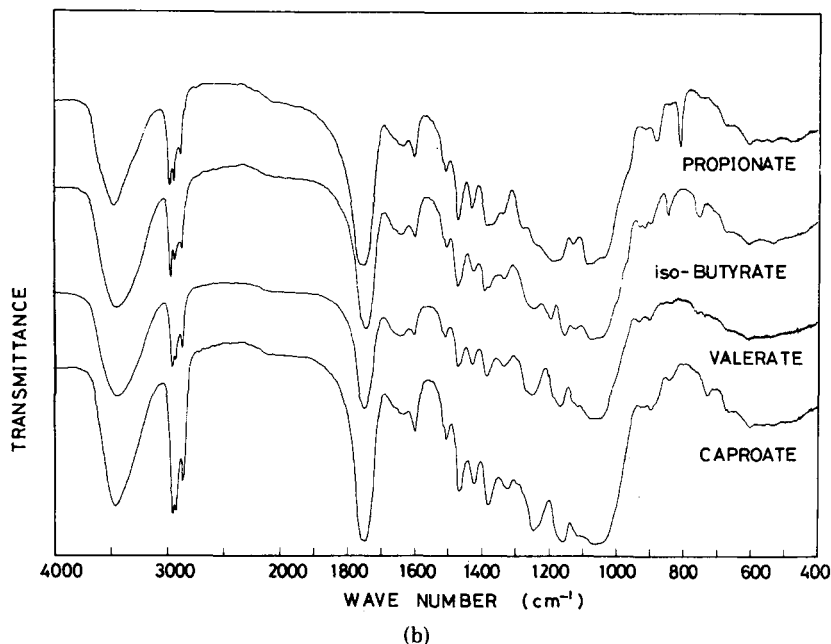
PROPIONATE

iso-BUTYRATE

VALERATE

CAPROATE

Fig. 9. (*Continued from previous page*)

Effect of the Presence of N_2O_4 in the Reaction Medium

Figure 10 illustrates log–log plots of the degree of esterification versus the reaction period for lauroylation of wood with lauroyl chloride in reaction media with and without N_2O_4. The curve for the reaction without N_2O_4 has two parts: an initial portion with greater slope for a reaction period less than 600 min, and a second portion of obviously lesser slope for a higher degree of lauroylation. On referring to the work of Conrad et al.,[16] it can be stated that the initial portion corresponds to the substitution of accessible hydroxyl groups in the amorphous regions as well as simultaneous and autocatalytic reactions in the crystalline
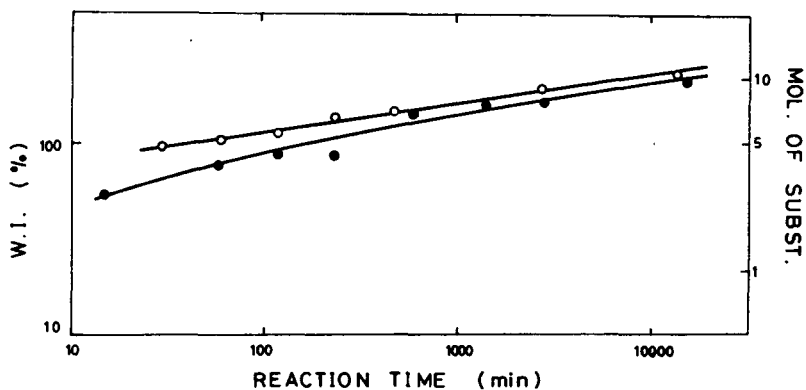

Fig. 10. Rates of lauroylation of wood with lauroyl chloride in reaction medium with or without N_2O_4: (O) in N_2O_4–DMF–pyridine medium; (●) in DMF–pyridine medium. Reaction conditions: wood meal, 1.3 g; N_2O_4, 6 moles per mole glucose unit or zero; DMF, 25 ml; pyridine, 25 ml; lauroyl chloride, 50 ml; reaction temp., 25°C.

regions; the subsequent lower rate of reaction represents esterification after the conclusion of decrystallization of the cellulose I structure.

Thus, the change in the rate of lauroylation with reaction time can be interpreted as an indication of the loss of cellulose I crystal structure from the sample. A theoretical explanation was given in the literature[16] for the fact that the decrease in the reaction rate occurs at the conclusion of decrystallization of the cellulose I structure. With this in mind, it is interesting to note in Figure 10 that the slope of the curve for the second reaction process coincides well with that for the reaction in the N_2O_4–DMF–pyridine medium.

The curve for the reaction in the medium containing N_2O_4 is linear over the whole range of reaction periods and does not have any inflection point. Furthermore, the absolute amount of the lauroyl group substituted is considerably larger than that attained during the reaction without N_2O_4 throughout the whole reaction process. Therefore, it can be stated that the presence of N_2O_4 causes the overall decrystallization of wood, and this is followed by the esterification involving the replacement of hydroxyl by lauroyl groups in the amorphous regions.

These arguments are supported by a comparison of x-ray curves for the reaction products prepared in the media with or without N_2O_4 (Fig. 11). The lateral order of the cellulose structure disappears completely in lauroylated wood from the earliest stage of the reaction in the N_2O_4–DMF–pyridine medium, showing that uniform substitution of the lauroyl group along the cellulose chain occurs from the beginning of the reaction and results in a permanent decrystallization with a small incorporation of the blocking group. In contrast, the diffraction due to the cellulose I structure remains even in the considerably lauroylated wood obtained after 240 min of reaction in the medium without N_2O_4.
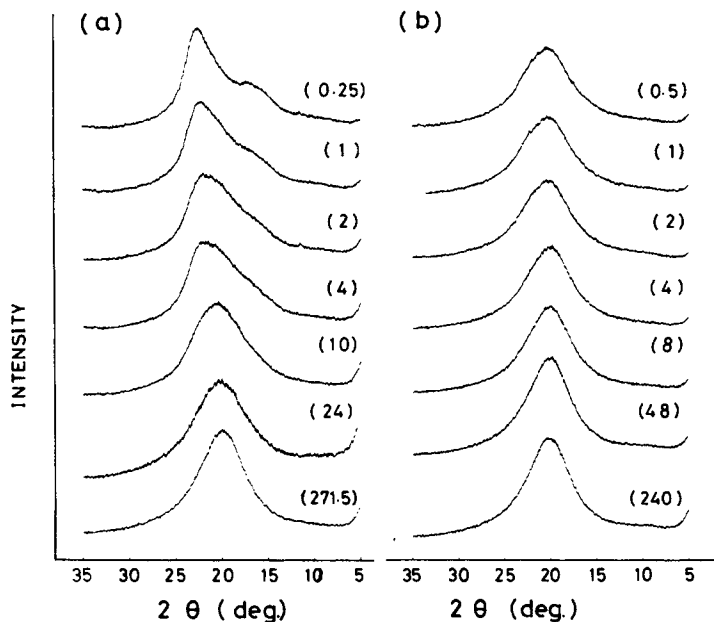

Fig. 11. X-Ray diffraction curves of wood lauroylated with lauroyl chloride in reaction medium (a) without or (b) with N_2O_4. Numerical values in parentheses represent reaction time (hr).

*Esterification of Wood with a Series of Acid Chlorides from Caproyl to
Stearoyl in N_2O_4–DMF–Pyridine Medium*

Using the same reaction conditions (wood meal, 1.3 g; N_2O_4, 6 moles per mole glucose unit; DMF, 25 ml; pyridine, 25 ml; acid chlorides, 0.22 mole; 25°C; 240 hr), a series of aliphatic esters of wood from caproate to stearate were prepared and the results are shown in Table I. It is evident from the table that the substituent molality attained with the esterified wood is not dependent on the acid chloride.

It can be concluded that the acid chlorides are more effective than the acid anhydrides as acylating agents and that, although no difference in reactivity can be recognized among the acid chlorides, the reactivity decreases with increase in the number of carbon atoms in the corresponding acyl group among the acid anhydrides.

In connection with these facts, the following explanation can be offered. In the first place, acid chlorides form an acyl pyridinium intermediate, $(Py^+COR)Cl^-$, with pyridine, participating in the esterification directly. The equilibrium lies far to the side of the formation of the intermediate, which facilitates the rapid progress of esterification. On the other hand, the equilibrium constant for the formation of an acyl pyridinium salt, $(Py^+COR)RCOO^-$, from the acid anhydride and pyridine is small. In connection with the aforesaid fact that the rate of esterification with the acid anhydride decreases with increase of the number of carbon atoms of the acid, the following effects can be considered: (1) The pK_a value for the acid anhydride slightly increases as the acid becomes a higher molecular weight acid, reducing the rate of esterification. (2) The polarity of the reaction medium gradually decreases with increase in the number of carbon atoms in the alkyl group of the acid anhydride. (3) The difficulty of the diffusion of the acid anhydride into the wood sample increases with increase in the molecular volume of the acyl group. On the other hand, in the case of the acid chloride, the formation of the acyl pyridinum salt is nearly quantitative, which raises the polarity of the reaction medium, increases the rate of esterification, and equalizes the reaction rate irrespective of the number of carbon atoms in the acid chloride utilized.

Although the above arguments are concentrated on the acetylation of cellulose within the wood cell wall, the hydroxyl groups of lignin and hemicellulose are considered to be acylated by these reactions. These points together with the effect of some mild pretreatment for breaking down the network structure of lignin on the acylation is being investigated and will be reported later.

TABLE I
Degree of Esterification of Wood with a Series of Acid Chlorides from Caproyl to Stearoyl in
N_2O_4–DMF–Pyridine Medium

Acid chloride	No. of C atoms	Weight increase, %	Molarity of substituent
Caproyl	6	123.5	10.6
Capryloyl	8	151.8	10.5
Caprinoyl	10	162.5	9.4
Lauroyl	12	221.6	11.1
Palmytoyl	16	217.4	8.5
Stearoyl	18	260.4	9.2

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