Chapter 3: Submitted to *Cellulose*

About the Depolymerization of Cellulose Propionate to Segments with low DP

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Abstract:

Low molecular weight cellulose propionate (CP) segments were synthesized by HBr hydrolysis under esterification conditions using either a commercial CP with residual hydroxyl groups (DS_{OH} ca. 0.4) or a tripropionate (CTP). The hydrolysis using CTP yielded segments having a minimum DP of as low as 7, whereas the hydrolysis of the commercial CP resulted in segments having a minimum DP of 50. Differences were also seen in the rate of depolymerization and the Mark-Houwink constant, which declined from 1 to 0.6 below DP 100 and 30 for commercial CP and CTP, respectively. The results are consistent with the hypothesis that branches are formed by transglycosidation, when OH-containing cellulose derivatives are hydrolyzed with HBr in aprotic solution.

Introduction:

We have previously reported on the hydrolysis of cellulose propionate to mono-functional polymer segments with degrees of polymerization (DP) ranging from five to fifty[1]. Short-DP cellulose propionate segments are potentially useful as components of multi-block copolymers[2,3]. The cellulosic segments potentially contribute to polymer properties through their high crystallinity, high melting temperature, high melt viscosity, and potential biodegradability (following deacylation).

Our previous synthesis protocol had been adopted from Mezger and Cantow[4] who had reported on the HBr-mediated hydrolysis of cellulose propionate to monofunctional cellulose ester segments in the presence of propionic anhydride. Although this method had been described as “not satisfactorily applicable to cellulose triacetate, [it] was found to be suitable to convert even incompletely substituted commercial cellulose propionates (DS = 2.7) into the desired 1-monobromo cellulose perester”[4]. In further studies conducted since the publication of our previous report, we have noticed that the cellulose propionate hydrolysis with HBr is subject to considerable variability and unpredictability in terms of target DP when certain grades of commercial cellulose propionate are used as starting material. These grades differ primarily in degree of substitution; their combined ester content rarely exceeds 2.7 which leaves 0.3 (or more) positions per anhydroglucose unit with their original OH-functionality[5]. Since transglycosidation is a common observation with hydroxy-bearing carbohydrates when glycosyl halides are present in the aprotic solvent[6,7], suspicion of uncontrolled branching arose. Although we had been aware of the fact that commercially available cellulose propionate had degrees of substitution (DS) lower than the theoretical maximum (3.0), we had relied on the presence of the propionic anhydride in the reaction neutralize any available free OH group before if could interfere with the hydrolysis. However, repeated problems with repeatability convinced us to re-examine the potential influence of transglycosidation side reactions on CP hydrolysis.

Experimental:

Materials:

Commercial cellulose propionate (product type CAP-482-0.5, 1.2 wt. % acetyl and 47 wt. % propionyl as reported by the supplier) was obtained from Eastman Chemicals, Kingsport, TN. Tripropionate was obtained by perpropionylation of the commercial product using propionic acid and propionic anhydride[8].

Hydrolysis reaction: Cellulose propionate hydrolysis was carried out in accordance with the earlier study[1] with minor modifications. Typically 10g cellulose propionate dissolved in 100 mL anhydrous dichloromethane was cooled to 0°C in an ice bath. Once that temperature was reached, propionic anhydride (20 mL) and a 33% solution of HBr in acetic acid (50 mL) was added to the closed and stirred flask using a syringe. The addition was slow enough so that the temperature was kept at 0°C. Duration of the reaction depended on the degree of polymerization desired and varied between 1 and 25 hours. Reactions longer than 12 h were kept at 0°C for 12 hours before being allowed to rise to room temperature for the remainder of the reaction. After that, the cold solution was precipitated into a cold suspension of aqueous ethanol and $NaHCO_3$, from which the solvents were evaporated and the solids were taken up in chloroform and water. The organic phase contained the hydrolyzed 1-monofunctional cellulose perpropionate which was isolated by dissolution in acetone and precipitation using water as non-solvent. By heating the concentrated acetone / water solution until it became clear, and by subsequently cooling it to room temperate, the 1-monohydroxy cellulose propionate precipitated as a fine powder that was filtered and dried.

Perpropionylation: The statistical F-esters may subsequently be perpropionylated. Typically, a 5% solution of the starting material is prepared in a 1:1 solution of acid and anhydride using a round bottom flask. Sodium alkanoate (0.3 eq M^{-1} of anhydride) is then added. The solution remains at room temperature while stirring, before it is heated to a boil for 2 hours. The mixture is then cooled to room temperature and precipitated into ten-fold excess of 0.1% HCl. The product is filtered, washed with water, and dried under vacuum.

Molecular weight determination: The molecular weights, polydispersity and Mark-Houwink exponential factor were determined by GPC using a differential viscosity detector (Viscotek Model No. 100) and a differential refractive index (concentration) detector (Waters 410) in sequence. The system was controlled by Viscotek software (Unical GPC software, Version 3.02). The materials were dissolved in THF (approximately 10% solution concentration) and analyzed using a high pressure liquid chromatography system based on three Waters Ultrastyragel columns with pore sizes of 10^3, 10^4 and 10^5Å. The columns and the detectors were heated to 40°C. The solvent was freshly degassed and kept constantly under a helium atmosphere. Narrow molecular weight polystyrene standards were used to establish a universal calibration of the GPC columns.

Results and Discussion:

The commercially available cellulose propionate had reported propionate / acetate contents of 47 / 1.2 % corresponding to a combined degree of substitution of 2.6. The FTIR spectrum (Figure 1) revealed a significant OH-stretch around 3400 cm^{-1} that disappeared following perpropionylation with propionic anhydride using pyridine as catalyst. The secondary esterification reaction proved not to affect the molecular weight of the cellulose ester. A minor increase in molecular weight (M_n) of 3000 daltons from 69000 to 72000 daltons was determined which was consistent with the expected weight gain during perpropionylation (Table 1).

When the re-propionylated cellulose propionate sample (tripropionate, CTP) was depolymerized in comparison to the commercially available product (CP), cellulose propionate samples were isolated that had molecular weights which declined in relation to hydrolysis time (Figure 2). The data clearly show that CTP and CP follow two different hydrolysis curves with reaction time under otherwise identical conditions. CP shows a dramatically slower loss of molecular weight, and a significantly higher "level off" DP than the CTP-preparation.

Differences were also observed in the Mark Houwink exponential factor a for the different samples (Figure 3). When a was plotted against DP_n, two different relationships emerged for CP and CTP. The data indicate that CTP retains an a-value of around one for all but the very lowest-DP cellulose ester sample. CP, on the other hand, revealed low a-values at much higher DPs. It is well known that a is an expression of polymer shape as well as backbone rigidity, and that a is highly sensitive to branching[9]. The decrease in a at low molecular weights is consistent with the loss of backbone rigidity for small segments. The decrease in a at higher molecular weights, however, can be attributed to the formation of branches during the hydrolysis reaction. This is consistent with transglycosidation in accordance with the reaction scheme shown in Figure 4. It must therefore be concluded that HBr-depolymerization is not applicable to commercial cellulose propionates for the formation of mono-functional linear segments of low DP, but that this reaction requires cellulose tripropionate.

Conclusions:

Cellulose esters (and probably all other cellulose derivatives with degrees of substitution of less than 3.0) are prone to the formation of branched derivatives when hydrolyzed with HBr in aprotic solvent. This side reaction inhibits the formation of cellulose ester segments with DPs below approximately 50.

The predictable formation of cellulose ester segments with DPs ranging from five to fifty requires the use of peracylated cellulose ester products and cannot be achieved using commercial grades.

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Table I: Starting materials for cellulose propionate hydrolysis

Sample designation	DS_{OH}	Molecular weight[1], M_n, daltons	Mark Houwink exponential factor
CTP	trace[2]	69000	1.04
CP	0.4[3]	72900	0.94

[1] determined by GPC

[2] identified by FT-IR using the ratio of the carbonyl peak and the hydroxyl peak; after perpropionylation only a trace of the hydroxyl peak is found

[3] calculated from propionate (47%) and acetate (1.2%) contents as stated by manufacturer (Eastman Chemicals, Kingsport, TN)

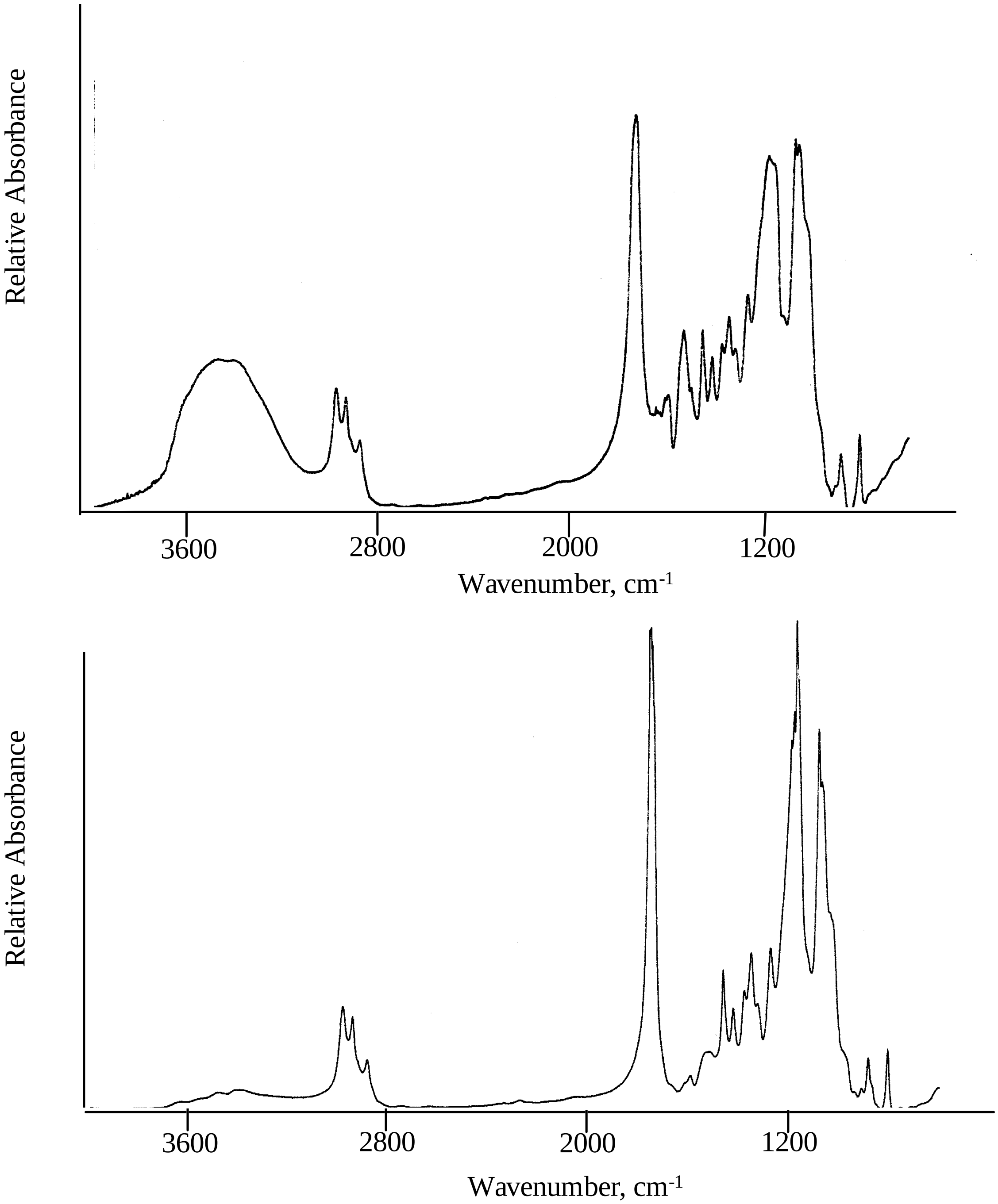

Figure 1:
FTIR spectra of commercial cellulose propionate (top) and of perpropionylated CTP (bottom). The hydroxyl strech around 3400 cm^{-1} indicates the presence of hydroxyl groups.

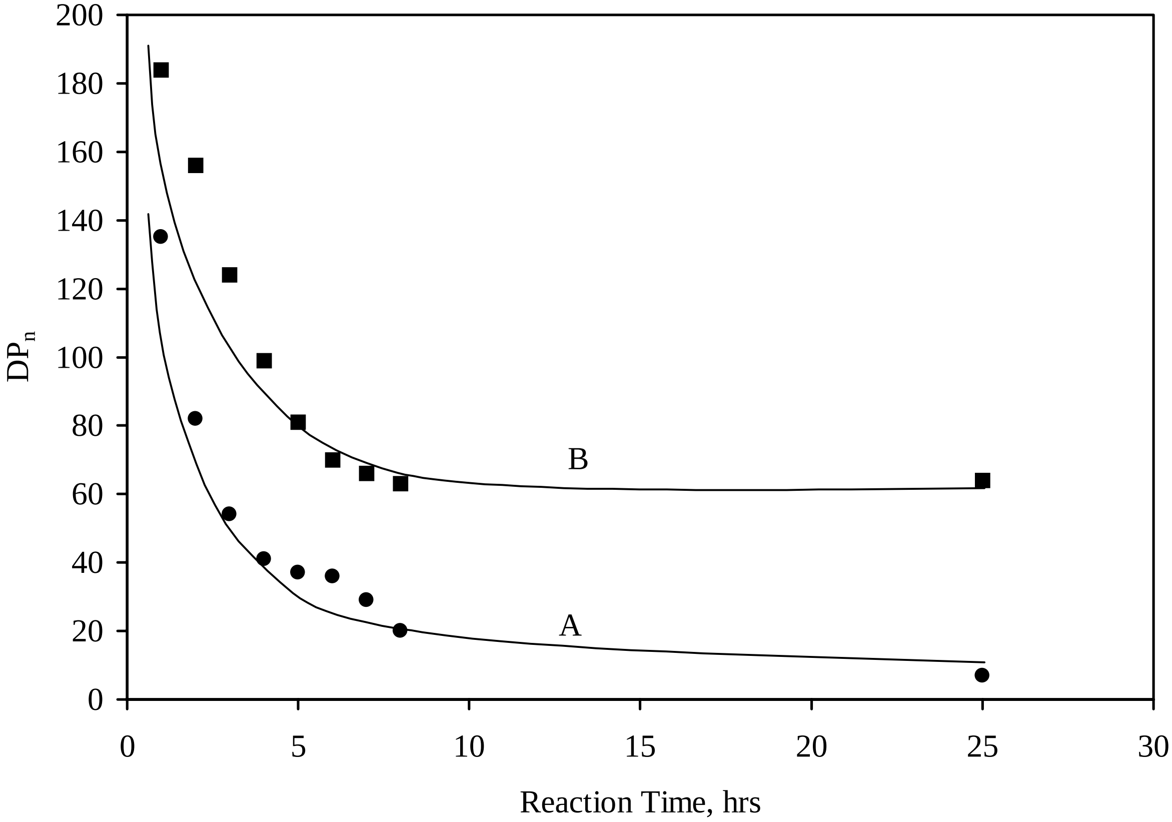

Figure 2:
DP values of CP segments after hydrolysis of perpropionylated CTP (A), and of commercial CP (B), in relation to hydrolysis time.

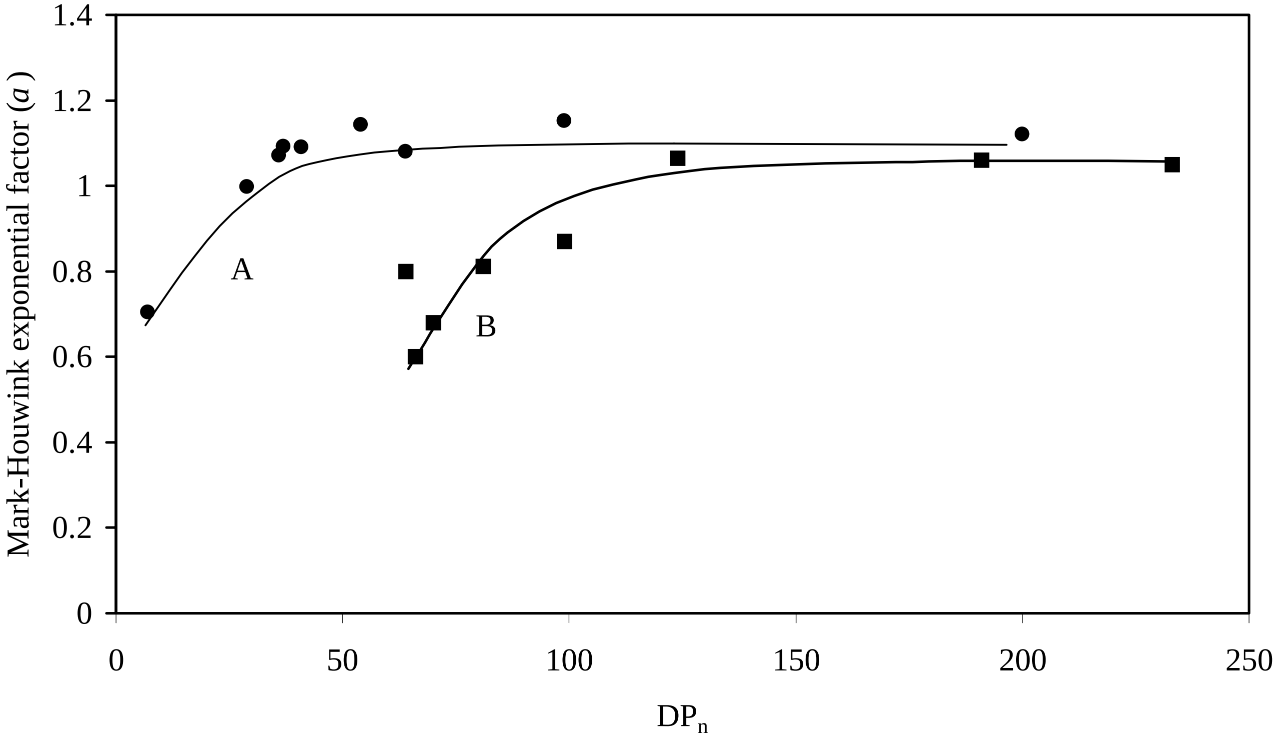

Figure 3:
Mark Houwink exponential factor *a* of CP segments after hydrolysis of perpropionylated CTP (A), and of CP (B), in relation to DP_n.

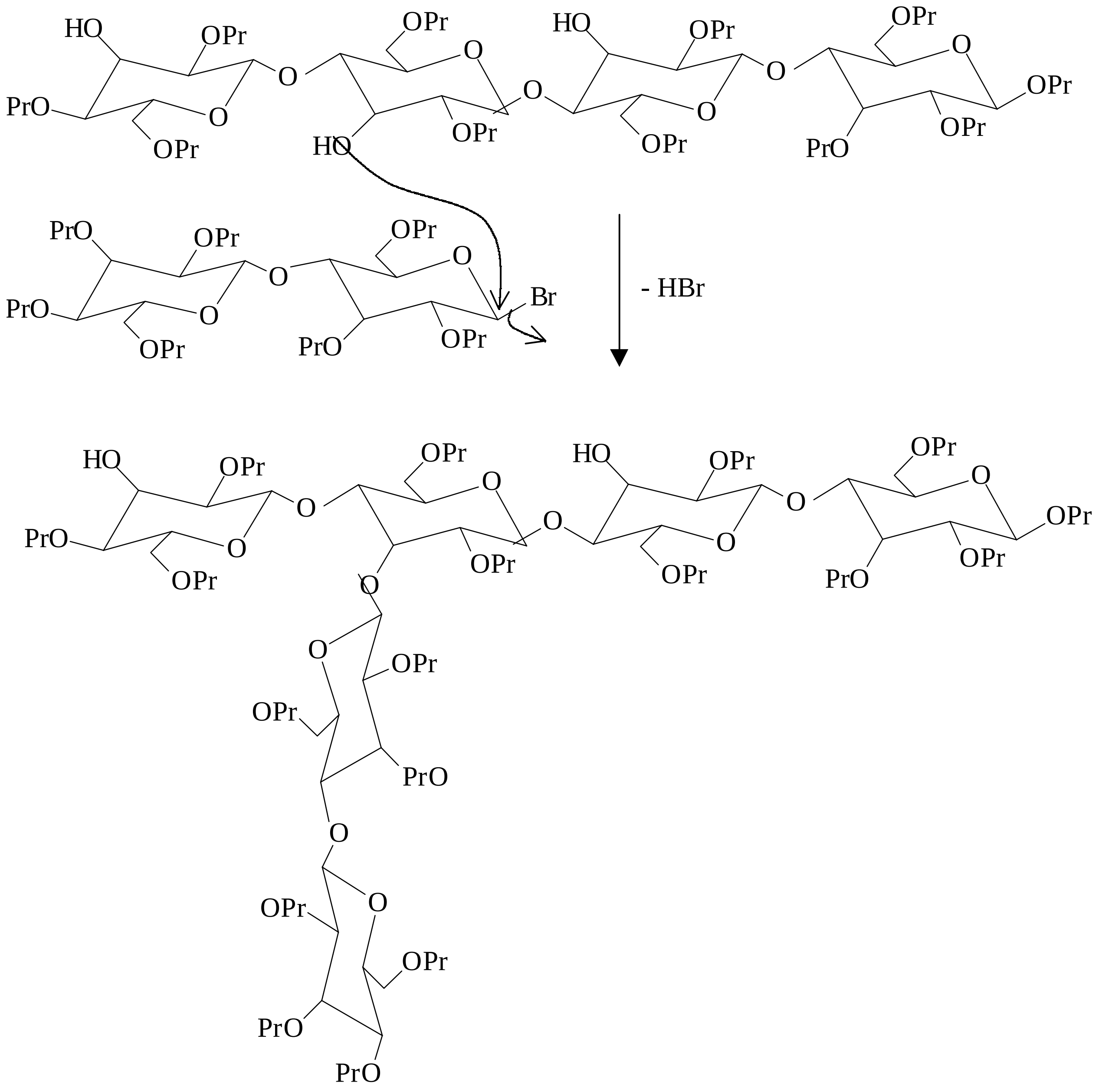

Figure 4:
Hypothetical reaction scheme of commercial-grade cellulose propionate during HBr-depolymerization. The initial depolymerization provides glycosyl bromides which subsequently participate in branching. Pr indicates propionyl groups.