VARIATION OF PERFORMANCE PROPERTIES OF CELLULOSE BY CHEMICAL TRANSFORMATION

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Abstract - Chemical transforming of the macromolecule as a means of changing physical and performance properties of polymers is rather an exception with synthetic polymers - copolymerisation being here more suitable in most cases -, but nearly always is the only choice with natural polymers like cellulose. After mentioning briefly some technological relevant examples of modifying the chemical structures of synthetic polymers like PVC or copolymers of ethylene by chemical reactions with the macromolecule, a survey is given on the present state of changing the product properties of cellulose by chemical transformation covering especially the fields of cellulose fibres, cellulosic membranes, and water-soluble or water-swellable synthetic gums like cellulose ethers. With the latter, the influence of DS and substituent distribution on solubility is stressed and demonstrated by some of our recent results. Finally, connections between cellulose chemistry and polysaccharide chemistry in general are considered with regard to modification, characterization and application of water-soluble products.

INTRODUCTION

In the field of large-scale polymers for plastics, elastomers, coatings and synthetic gums, a major goal of today's research and development is an increased "utility value" and a better adaption of material properties to specified end-use demands, in order to make a better use of the limited resources available, and to cope with consumer's needs and wishes. This variation of material properties like breaking strength, toughness, heat resistance, or binding capacity for water, may be achieved either by modifying the physical structure alone, or by a change in chemical structure of the polymer usually including also changes in supramolecular or morphological structure. Well-known examples in the fibres field are the dependence of stress_strain curves of viscose rayon on spinning conditions via a changing supramolecular structure on the one hand and the influence of comonomers on textile performance of acrylic fibres on the other.With large-scale synthetic polymers, changes in chemical structure are usually performed by copolymerization, chemical transformation of the macromolecule being an exception rather than a rule. Relevant examples of the latter pathway are the chlorination of PVC or of polyethylene. Grafting, for example, of styrene to NBR-latex or of vinyl chloride to an ethylene-vinylacetate copolymer may be considered as a limiting case of chemical transformation of the macromolecule.

With polymers preformed by nature, i.e. polyisoprenes, polysaccharides, lignin, proteins and nucleic acid, chemical transformation of the macromolecule is the only choice of changing material properties via the chemical structure. Even though several technological and economic problems arise in connection with chemical reactions on the macromolecule, this way is successfully practised since about one century, especially with cellulose.

It seems reasonable, therefore, to limit the scope of this context to recent results and achievements in changing material properties of cellulose by chemical transformation of this macromolecule. Referring to this particular polymer, some general features of heterogeneous reactions with polymers will be discussed, and the versatility of the cellulose molecule in preparing fibres, films, artificial membranes, sorbent powders, and water-

soluble synthetic gums will be demonstrated, considering some recent re-
sults of our own especially in the field of membranes, sorbents and water-
soluble cellulose ethers.

SOME REMARKS ON CHEMICAL TRANSFORMATION OF CELLULOSE

The anhydroglucose units of cellulose are linked by 1-4-β-glucosidic bonds
susceptible to acid or enzymatic hydrolysis, and to each monomer unit 3
hydroxyl groups are attached which may be esterified, etherified or oxidized.
Cellulose derivatives thus obtained often are products of technical im-
portance, but also may serve as intermediates for subsequent steps of reac-
tion. Fig. 1 gives some examples from Rogovin's comprehensive work in this
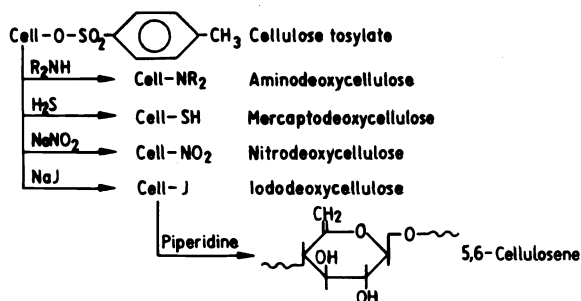

Fig. 1. Examples of multi step reaction on the cellulose molecule.

field (1). If no special precautions are taken, most of these cellulose re-
actions of the "covalent type" proceed with considerable chain-length degra-
dation, and minimizing this degradation often is a point of interest in to-
day's cellulose derivatives manufacture, especially in the field of water-
soluble, high-viscosity ethers and esters.

As a special type of covalent cellulose reactions radical grafting at the
cellulosic OH-groups may be mentioned. This grafting process is initiated
either by high energy radiation or by redox reaction.

Besides this covalent type of cellulose reactions, technologically relevant
changes in cellulose properties may be achieved also by formation of tran-
sient addition compounds or of complexes of different binding strength be-
tween cellulose and low molecular compounds.

Mercerisation of cotton via the addition compound alkali cellulose as an in-
termediate is a classical example, and the array of metal complex solvents,
as well as the non-aqueous cellulose solvents based on EDA-complex forma-
tion (Fig. 2) may be mentioned as more recent achievements in this field of
growing interest.

All the chemical transformations of cellulose have to start in a heterogene-
ous system with the reaction product either still comprising a separate
phase, as for example in crosslinking or grafting reactions with cellulose
fibres, or with the product being dissolved in the medium, as in a wet xan-
thation process. Due to this heterogeneous course of reaction, the kinetics
and the product properties are influenced by some additional parameters,
i.e.

- the morphology of the cellulose fibre, i.e. lateral order, porosity and
  surface structure, gross morphology

- the reaction medium, via changes in cellulose hydroxyl group reactivity
  and via the state of swelling

- the molar volume of the reagent in relation to pore size distribution

- the rate and the evenness of reagent distribution on macroscopic and on
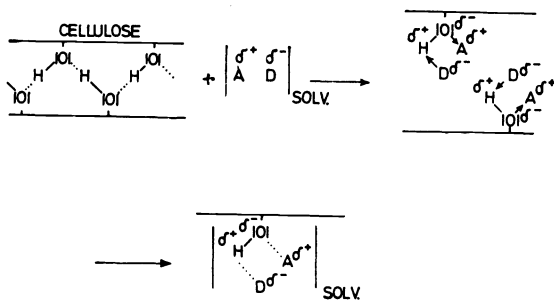 microscopic level.

Fig. 2. Scheme of the EDA-complex formation on the cellulose macromolecule.

All of these parameters may have an effect on the interrelation between transformation and diffusion steps of heterogeneous cellulose reactions, and all of these parameters may change themselves during the course of the reaction. Due to this complexity, a quantitative mechanism-based modelling of heterophase cellulose reactions is up to now an exception rather than a rule. Technologically relevant parameters like choice of suitable pretreatments of cellulose and of suitable reaction media, or of an optimum reagent dosage rate in connection with mechanical stirring and kneading of the system have still to be done mainly on empirical or semiempirical basis. Only qualitative statements are possible with regard to the significance of the numerous parameters mentioned above and these statements are valid only for the specific cellulose reaction in question. Thus, for example, it may be concluded from our work that the influence of lateral order and gross morphology, i.e. the difference between a strictly homogeneous and a strictly heterogeneous course of reaction on the rate constant, increases significantly with decreasing state of swelling in the reaction medium and also with increasing molar volume of the reagent with a cellulose sample of given morphological structure (Table 1).

TABLE 1. Relative rate constants

Reaction	Swelling state	Heterogeneous reaction	Homogeneous reaction
Carboxy-methylation	strong	50	100
Cyano-ethylation	medium	10...25	100
Enzymatic hydrolysis	very small	0,01	100

Besides their relevance in determining the course of reaction the parameters listed above have a bearing on product properties, especially via the substituent distribution and the microscopic homogenity of chemical composition. Fig. 3 demonstrates the different modes of an unequal distribution of substituents in partly substituted cellulose derivatives. Particularly, the solubility properties of cellulose ethers and esters depend largely on substituent distribution along and between the chain.

Obviously further progress in elucidating and modelling of heterogeneous cellulose reactions is closely related to progress in cellulose analysis,
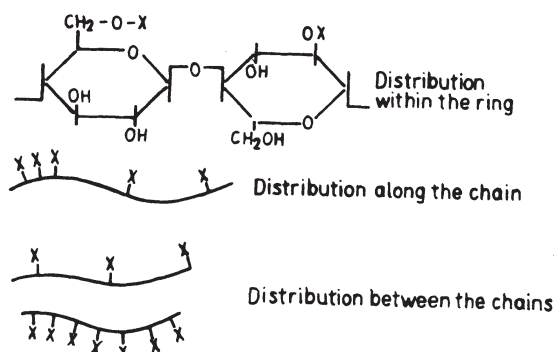
Fig. 3. Modes of unequal substituent distribution in cellulose
derivatives.

comprising in a rather complex manner chemical and physical methods. Thus,
we urgently need better methods for characterizing substituent distribu-
tions along and between the macromolecules and also – on macroscopic scale –
between individual particles. Transfer and adaption of knowledge in charac-
terizing synthetic copolymers and adaption of modern methods of surface
analysis like ESCA may be of advantage here.

These methods of chemical analysis definitely need to be supplemented by
morphological methods especially SEM- and EDAX techniques, as even re-
actions maintaining the macroscopic fibre structure, like an alkali treat-
ment of cotton linters, may be accompanied by significant changes in mor-
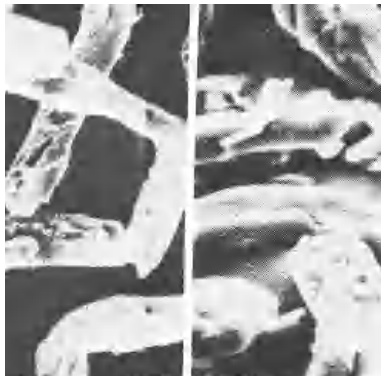phology that (Fig. 4) distinctly affect, the performance properties of the
reaction product.

Fig. 4. SEM-micrographs of cotton linters powder before and
after alkali treatment.

SURVEY OF RECENT DEVELOPMENTS IN CELLULOSE PRODUCTS ACHIEVED BY
CHEMICAL TRANSFORMATION

Of the major fields of today's cellulose application, i.e.

– paper

– chemical and natural fibres

– films and membranes

– sorbents and cellulose powders

– soluble synthetic gums, based on ethers and esters of cellulose

- chemicals obtained by degradation of cellulose and hemicellulose

the first and the last one may only be mentioned here: Low molecular weight
degradation products like glucose are outside the frame of this lecture
dealing with the still intact cellulose macromolecule. Recent developments
in the paper field mainly proceed along the lines of processing the ligno-
cellulose moiety in an optimum way and of blending cellulose with synthetic
polymers. Chemical transformation of delignified paper pulp like grafting
or surface oxidation so far are not practised on large scale due to eco-
nomical reasons, in spite of potential gains in product quality. A survey
of the other classes of cellulose products mentioned above will be centered
on the question:

"What has been new in products and product properties and what is the
rating of the different ways to arrive at new products?", i.e.

- blending of cellulose with other compounds

- changing the morphology of cellulose products without permanent chemical
  transformation

- changing the chemical structure of cellulose by new processes of trans-
  formation.

In the field of textile fibres, chemical transformation may be employed
either to adapt properties of natural or man-made cellulose fibres to spe-
cial consumer's demands, or to develop new technologies for processing
cellulose to man-made fibres. Regarding the first point, a lot of experimen-
tal results have been reported in the past few years on cross-linking and
grafting of cotton and rayon staple in order to improve permanent press
and wrinkling behavior, or to convey special properties like flame-retar-
dancy or fungicity to the finished goods. Particularly with regard to
flame-retardancy, a covalent binding of hetero-elements like phosphorus to
the cellulose chain seems to be a promising approach, which even may be
combined with cross-linking to improve wash- and wear properties. An exam-
ple for changing the stress-strain curve and thus the textile performance
properties of cotton via a transient chemical transformation is the "Pro-
Grade"-process [R] : By treatment with liquid ammonia an addition compound
is formed, which on decomposition effects a change in H-bond structure and
lateral order of the cellulose. Thus, a change in mechanical properties is
achieved by a change in cellulose physical structure without permanent
aerivatization, but this change is evoked by transient chemical trans-
formation.

In order to avoid ecological hazards of the viscose process, much research
effort has been spent in the last two decades to find alternative pro-
cesses for spinning man-made cellulose fibres by using either non-aqueous
solvents for cellulose, or alkaline aqueous solutions of low substituted
cellulose ethers like hydroxyethyl or cyanoethyl cellulose. Referring to a
recent review of ours (2) in this field, it must be concluded with regard
to the performance properties of the filaments thus obtained that fibres
spun from low-substituted cellulose ethers are definitely inferior to vis-
cose rayon in wet-state properties unless a subsequent cross-linking is in-
cluded into the process. Filaments obtained from non-aqueous cellulose so-
lutions may reach but not surpass the quality level of viscose rayon
(Table 2).

Similar conclusions can be drawn from lab-scale results of spinning regen-
erated cellulose fibres from various aqueous metal complex solutions as
compared to viscose or cuprammonium rayon, as well as for filaments spun
from various cellulose derivatives like a highly substituted cyanoethyl
cellulose as compared to acetate rayon. Leaving aside all economical,
ecological and technological consideration it must be stated that in spite
of the host of reactions known today for derivatizing or dissolving cellu-
lose so far no alternative pathway to man-made cellulose fibres of better
performance properties than those of the one-century-old viscose rayon,
cuprammonium rayon and acetate rayon has been found.

In the field of cellulose-based films and membranes recent progress in per-
formance properties of commercial products was achieved mainly along con-
ventional lines, i.e. by optimizing the physical structure via technolog-
ical parameters or by new laquer or coating composition and not by apply-
ing new principles of chemical transformation.

Our recent results with model films of carboxymethyl cellulose (CMC) demonstrated the variability of mechanical and physicochemical data of a cellulose product by an ionic reaction, i.e. by exchanging H^+ by different cations in an H-CMC film subsequent to casting from an alkaline aqueous CMC solution into an acid coagulation bath (Table 3). On the other hand, a tran-

TABLE 2. Mechanical properties of man-made cellulose fibers obtained by different processes (literature data)

Cellulose solution	Tenacity / N/tex / Conditioned	Wet	Elongation / % / Conditioned	Wet
Viscose (regular rayon)	0,13-0,21	0,09-0,16	14-25	18-35
Viscose (high wet modulus rayon)	0,30-0,70	0,22-0,53	6-14	9-18
Cellulose-N_2O_4-DMF	0,15-0,32	0,13-0,21	5-23	10-15
Cellulose-CH_2O-DMSO	0,11-0,25	0,09-0,15	4-18	4-18
Cellulose-N-ethylpyridinium chloride-DMF	0,12	-	10	-

TABLE 3. Strength, swelling and sorption data of CMC-model-films after ion-exchange with different metal ions (DS of film = 0,50)

Counter-Ion	Tenacity Conditioned / N/tex /	Water Retention Value / % /	DMSO Retention Value / % /	Water Vapor Sorption 65 % R.H./ 25 °C / % /
H^+	0,016	129	158	14,1
Na^+	0,016	1225	18	22,0
NH_4^+	0,017	1400	22	18,6
Ca^{++}	0,021	1300	20	21,0
Zn^{++}	0,022	860	18	19,0
Pb^{++}	x	59	20	10,5

x - too brittle to be measured at comparable conditions

sient xanthogenation of CMC with subsequent splitting off the xanthogenate groups in the acid coagulation bath resulted in quite a different morphology of the film as compared to a sample coagulated directly from an alkaline CMC solution (Fig. 5). This difference in film morphology is reflected also by a difference in mechanical and physicochemical parameters of the two samples (tenacity without xanthation 0,014 N/tex, tenacity with xanthation 0,033 N/tex). By introducing carboxymethyl and xanthate groups into the cellulose matrix in different ways before coagulation casting a film from this solution, no significant difference in mechanical data has been found between films obtained by blending cellulose and CMC of DS = 0,6 and by applying a "copolymer" of cellulose and carboxymethyl cellulose with the same content of carboxylic groups in the film. From all these results it may be concluded that chemical transformation and variation of morphology have to be considered altogether in a rather complex manner in order to taylor material properties of cellulose products for a specific end-use, and
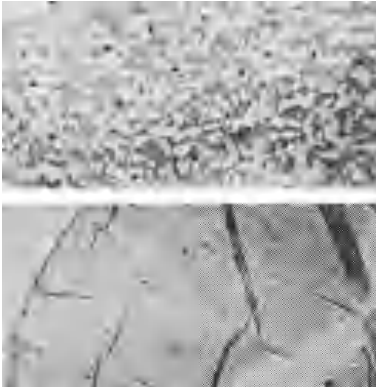
Fig. 5. Electron micrographs of H-CMC-film cast with and
without a transient xanthogenation.

that blending in some cases may be considered as an alternative to chemical
transformation.

Interesting problems in connection with chemical transformation and
morphology of cellulose may arise in application of artificial membranes in
biochemistry and medicine. Thus, it is still a point of discussion whether
a detrimental blood clotting activity of the membrane wall in haemodialysis
is to be minimized either by making a smoother membrane surface layer or by
introducing suitable anionic groups into the polymer chains of the membrane
wall.

The relevance of cellulose morphology with regard to material properties is
also shown by recent developments of cellulose powders for application in
chromatography, cosmetics and pharmacy. While selectivity in binding dif-
ferent substrates is determined by the substituent groups introduced into
the cellulose chain by chemical transformation – the array of cellulose ion
exchangers available now with carboxylic, sulphonic, phosphoric, amino and
ammonium groups available now giving due regard to this performance proper-
ties of cellulose sorbents in the chromatography column definitely is pri-
marily a matter of cellulose morphology; i.e. particle shape, particle size,
size distribution, porosity, and state of swelling under condition of use.
Fig. 6 gives an impression of this morphological variability of cellulose
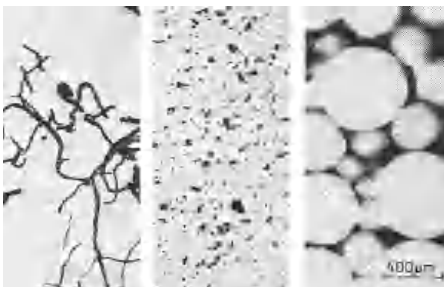

Fig. 6. Morphology of different cellulose sorbents (cellulose powder
obtained by mechanical desintegration, powder produced by heteroge-
neous acid hydrolysis with subsequent mechanical desintegration,
bead cellulose prepared by decomposition of a cellulose xantho-
genate solution under special conditions).

sorbents, comparing a cellulose powder obtained by mechanical desintegra-
tion,a powder produced by heterogeneous acid hydrolysis with subsequent me-

chanical desintegration and the "Bead Cellulose" ® of Štamberg (3) prepared
by decomposition of a cellulose xanthogenate solution under special condi-
tions. Further modification of sorbent properties is feasible via a change
in pore size and size distribution by action of a cellulolytic enzyme sÿs-
tem, as shown by Stamberg and us recently. All the products shown in the
foregoing slides are from a chemical point of view composed of the same sub-
stance i.e. cellulose. The array of different particle shapes and different
performance properties of these sorbents is the result of a suitable combi-
nation of steps of chemical transformation (xanthation, enzymatic or acid
hydrolysis) and mechanical treatment like milling in the solid state or
stirring in the state of solution.

A rapidly expanding area is the manufacture of water-soluble or water-
swellable derivatives and their application as non-toxic, versatile addi-
tives and auxiliary products. The main route to new products based on cellu-
lose ethers is the substitution of the anhydroglucose units with two or
three different groups varying in polarity or length of the side-chain.

Also successful efforts have been made to find new applications for the
"oldtimer" carboxymethyl cellulose, for example by manufacturing crosslinked
fibrous products for diapers of remarkable high swelling capacity, but
still sufficient dimensional stability in the wet state (4). User's demands
for high viscosity in rather dilute solution and for special rheological
properties in solution are being met now by new types of cellulose ethers
as well as by a new route to cellulose sulphate based on a non-aqueous
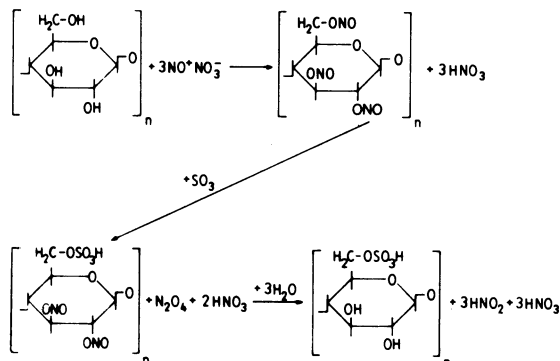solvent system (Fig. 7).

Fig. 7. Route to high viscosity cellulose sulphate.

This commercially expanding field of water-soluble derivatives and water-
swellable gels of cellulose simultaneously is a scientific challenge to
cellulose chemicals, as it

- provides an opportunity to apply new or hitherto unused cellulose reac-
  tions for modifying cellulose product properties

- stimulates research in cellulose structure and kinetics of heterogeneous
  reactions in order to find the best way of cellulose pretreatment for ob-
  taining a special, mostly a very homogeneous substituent distribution

- fosters new scientific and technological ideas of processing and after-
  treatment of the ether or ester subsequent to the chemical reaction step:
  this aftertreatment being often decisive for obtaining a product of ade-
  quate processability for the specific end-use in question.

The importance of substituent distribution in determining solubility of i-
onic and non-ionic ethers of cellulose may be stressed by referring to our
results with cyanoethyl cellulose and its decomposition products. The for-
mation of cyanoethyl cellulose by Michael addition of acrylonitrile to cel-
lulose in an aqueous alkaline medium and routes of decomposition of this
derivative are summarized in Fig. 8. Cyanoethyl cellulose prepared in the
conventional way is not completely soluble neither in water nor in aqueous
alkali, in the range of DS from 0 to 3, and solubility in DMF or DMSO is
found only at very high DS above 2,5. By combining a decrystallizing pre-

Principal reaction

$$\text{Cell OH} + CH_2 = CH\ CN \underset{}{\overset{(NaOH)}{\rightleftharpoons}} \text{Cell OCH}_2CH_2\ CN$$

Side reactions

$$CH_2 = CH\ CN \xrightarrow[+H_2O]{(NaOH)} CH_2 = CH\ C\overset{\nearrow O}{\underset{\searrow NH_2}{}}$$

$$CH_2 = CH\ C\overset{\nearrow O}{\underset{\searrow NH_2}{}} \xrightarrow{+NaOH} CH_2 = CH\ COONa + NH_3$$

$$\text{Cell OH} + CH_2 = CH\ C\overset{\nearrow O}{\underset{\searrow NH_2}{}} \xrightarrow{(NaOH)} \text{Cell O CH}_2CH_2C\overset{\nearrow O}{\underset{\searrow NH_2}{}}$$

$$\text{Cell O CH}_2CH_2C\overset{\nearrow O}{\underset{\searrow NH_2}{}} \xrightarrow{+NaOH} \text{Cell O CH}_2CH_2\ COONa + NH_3$$

$$CH_2 = CH\ CN + H_2O \xrightarrow{(NaOH)} HO\ CH_2CH_2CN$$

$$2CH_2 = CH\ CN + H_2O \xrightarrow{(NaOH)} (NCCH_2CH_2)_2O$$
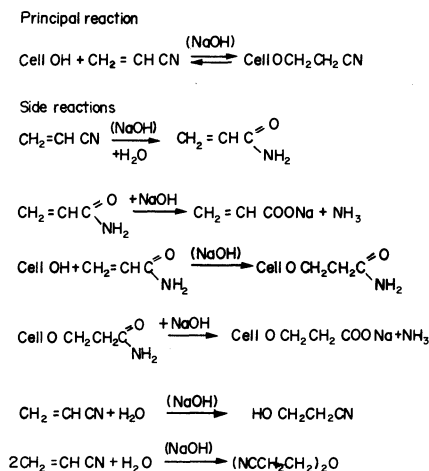
Fig. 8. Scheme of formation and decomposition of cyanoethyl cellulose.

treatment using ammonia or sodium hydroxide with a suitable course of the cyanoethylation reaction we succeded in preparing alkali-soluble and even water-soluble cyanoethyl cellulose in a one-step reaction, and also in low-ering the limiting DS for solubility in DMF or DMSO (Table 4). Obviously,

TABLE 4. Solubility of cyanoethyl cellulose prepared in diffe-rent ways

Preparation of the cyanoethyl cellulose	DS	Solubility
Without activation of pulp, heterogeneous cyanoethylation	0 - 2,2	insoluble in water insoluble in alkali insoluble in organic solvents
Pulp treated with li-quid ammonia, hetero-geneous cyanoethyla-tion	0,25-0,45	soluble in alkali
Homogeneous cyano-ethylation	0,7 - 1,0	soluble in water
Partly homogeneous cyanoethylation	>1,2	soluble in organic solvents like DMSO

the combination of pretreatment with the course of reaction employed re-sults in a rather even distribution of substituents, which therefore can act in an optimum way as "spacer groups" and thus promote hydration of the OH-groups no longer engaged and fixed in an H-bond system. By this way, dissolution in water is achieved by fixation of cyanoethyl groups to the chain in spite of their hydrophilic nature. Applying this principle of evenly distributed spacer groups to a hydrophilic substituent like the carb-oxyethyl group results in a water-soluble derivative even at a very low DS. Thus a carboxyethyl cellulose prepared by decomposition of cyanoethyl cellu-lose in a homogeneous reaction system proved to be alkali-soluble at a DS of 0,05...0,10 and water-soluble at a DS of 0,15...0,20, and showed a re-markable high viscosity in dilute solution, which may be connected with the strong tendency to aggregation of the cellulose chains carrying on the aver-age only one substituent groups per five to ten monomer units and thus be-ing the water-soluble cellulose derivative with the lowest DS hitherto re-ported (5). Besides their special rheological properties, these low-substi-tuted carboxyethyl celluloses show a remarkable high biodegradability by cellulolytic enzyme systems (6).

CONCLUDING REMARKS

Starting from some general considerations on reactions and on reactivity of cellulose this paper intended to give an information on recent developments in cellulose products, demonstrating the versatility of this polymer in making fibres, films, sorbents and water-soluble derivatives. It must be stressed, finally, that this variability in material properties primarily can be traced back to the suitability of the cellulose macromolecule for a host of permanent or transient chemical transformations, but that these chemical transformations always have to be considered in connection with changes in cellulose morphology in striving for better performance properties of cellulose products. This means that well-established chemical technologies of cellulose processing still offer chances to arrive at "new products" by changing product morphology via reaction parameters as demonstrated by HWM and polynosic rayon staple as recent products of the 100 years old viscose process. On the other hand, changes in morphology accompanying the chemical reaction may be an important approach or a handicap in large-scale practizing of cellulose reactions recently discovered or hitherto not used. Transient derivatization like formation of EDA-complexes or addition compounds as well as topochemical points of view may become more important in future cellulose chemistry not only due to the challenging scientific problems offered, but also in order to improve cellulose product properties by combining chemical and morphological transformations.

This need for a complex and synoptic consideration of chemistry and morphology is rather easily comprehensible for products applied in the solid state. But this point of view may be transferred also to derivatives applied in solution or as a gel, where even in a macroscopic homogeneous and transparent system an aggregation of cellulose chains may result in some kind of "morphology" which depends on DS and substituent distribution and which may strongly influence the performance properties.

Further progress in this field may be stimulated by applying recent results of characterizing synthetic copolymers to cellulose derivatives and by a more intense exchange of ideas and methods between cellulose research and the chemistry and physics of other polysaccharides.

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