Organic Solvents for Cellulose as a Biodegradable Polymer and Their Applicability for Cellulose Spinning and Derivatization

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ORGANIC SOLVENTS FOR CELLULOSE AS A BIODEGRADABLE POLYMER AND THEIR APPLICABILITY FOR CELLULOSE SPINNING AND DERIVATIZATION

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ABSTRACT

After some introductory remarks on cellulose as a renewable and biodegradable polymer and the relevance of new nonaqueous solvent systems for its processing, a survey is presented on the composition, the method of action and potential applications of these solvent systems, with a distinction between "derivatizing" and "nonderivatizing" solvent systems. The mechanism of dissolution is discussed with regard to interaction on the molecular level and with regard to the influence of cellulose physical structure. Among the systems considered for fiber spinning, the aminoxide-based solvent systems are given special attention. As another potential area of application, the use of nonaqueous solvent systems for performing regioselective derivatization at the cellulose molecule is presented briefly.

INTRODUCTION

After surviving more than one necrolog during this century, cellulose research and development has gained new impetus in recent years in connection with the actual problem of making better use of renewable resources, and also in connection with the worldwide search for biodegradable materials as a strategy for solving waste problems.

Among the main routes of cellulose processing to useful goods as schematized in Fig. 1, the transformation to threads and films via the state of solution and the
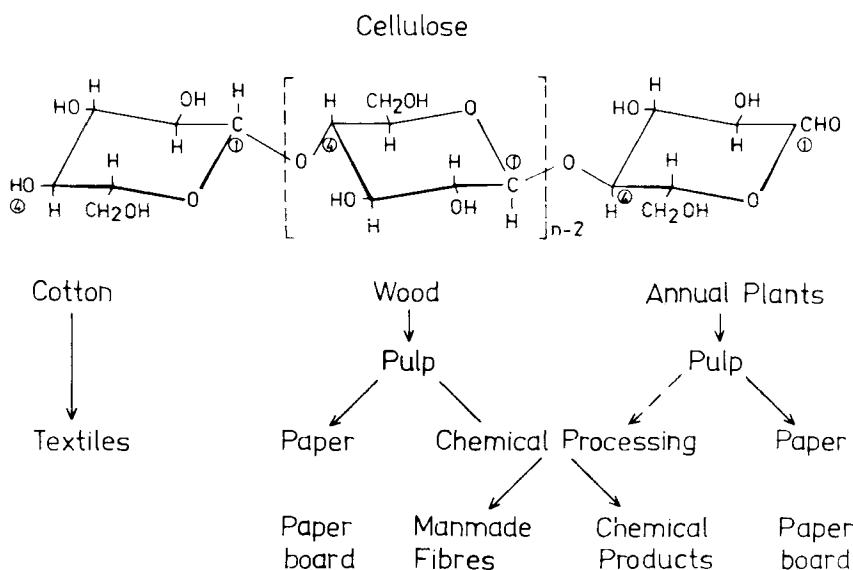
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FIG. 1.   Cellulose sources and cellulose processing (schematic).

derivatization to esters and ethers as commercial products fit into the frame of a polymer symposium, especially one dedicated to Herman F. Mark, and will be the topic of this lecture. It should be stressed that the textile industry cannot desist from cellulose-based man-made fibers for various reasons, and staple and filament are still produced worldwide at a level of millions of tons annually. Furthermore, native as well as regenerated cellulose is completely biodegradable by common, ubiquitous soil bacteria, and the same holds true for water-soluble cellulose derivatives of low to medium degree of substitution, such as commercial carboxymethyl cellulose.

Large-scale chemical processing of cellulose is performed mostly in aqueous systems. The most important example is the viscose process, which employs an aqueous alkaline solution of cellulose xanthogenate as the spinning dope and permits a remarkable versatility of textile thread properties, but is burdened with the well-known ecological hazards of CS_2 and H_2S. This situation promoted the search for alternative approaches to dissolve cellulose and transform it into threads or films, resulting in the development of numerous new, mostly nonaqueous solvent systems for cellulose and their testing in spinning processes. From a scientific point of view, the discovery of these new solvent systems, the elucidation of their mechanism of action, the results on structure formation of regenerated cellulose from these solutions, and last but not least the investigations on regioselective cellulose substitution at homogeneous conditions in these solvent systems can be envisaged as the most important contributions of cellulose research to polymer science in the last three decades.

A survey on the "state of the art" of developing and applying these new solvent systems for cellulose shall be presented. Regarding experimental results, only some arbitrarily selected examples can be considered here of the work of the cellulose

research group at the former Institute of Polymer Chemistry in Teltow-Seehof, which is now being continued within the recently founded Fraunhofer Institute of Applied Polymer Research.

OVERVIEW ON COMPOSITION AND ACTION OF "NEW" CELLULOSE SOLVENTS

With only one important exception, i.e., the so-called "carbamate process" [1], the solvents considered here are nonaqueous systems and in many cases even aprotic ones, composed sometimes of only one but mostly of two or more inorganic and/or organic compounds. From the chemist's point of view, it is reasonable to categorize the host of systems described up to now into "derivatizing" and "nonderivatizing" ones. Some examples of both classes are given in Table 1. Derivatizing systems exert their solvent action via the formation of covalent but unstable ethers or esters of cellulose, which are decomposed to "regenerated cellulose," usually cellulose II, by changing the pH and/or by turning from an aprotic to a protic system. Nonderivatizing solvents, on the other hand, dissolve the polymer by intermolecular interaction only; for example, by the formation of H-bond complexes.

The time required for dissolution and its completion varies widely depending on the solvent system and the physical structure of the cellulose sample. The N_2O_4/dimethylformamide system or N-methylmorpholin-N-oxide monohydrate, for example, dissolve even high molecular cellulose rather quickly, irrespective of physical structure, while the borderline solvent system methylamine/dimethylsulfoxide dissolves cellulose I samples of low and medium DP only.

As especially investigated by Schleicher, an activating pretreatment for loosening cellulose physical structure is suitable or even necessary with many of the nonaqueous solvent systems in order to obtain a solution free of native fiber fragments. According to Schleicher [2], there is no generalizable "optimal activation treatment" available, but the most appropriate technique must always be chosen in relation to the solvent system employed. Table 2 summarizes some activation techniques studied in connection with nonaqueous cellulose solvent systems. Figure 2 shows the solubility of two cellulose samples in binary mixtures of N-methylmorpholine-N-oxide monohydrate (NMMNO·H_2O) as the active solvent component and DMSO as the diluent, demonstrating that 1) here as well as in other cases an active solvent can be diluted with an inactive one without losing its ability to dissolve cellulose,

TABLE 1. Some Nonaqueous Solvent Systems for Cellulose

Derivatizing systems	Nonderivatizing systems
N_2O_4/DMF	N_2H_4
$NOSO_4H$/DMF	NH_3/NH_4SCN
$(CH_3)_3SiCl$/DMF	SO_2/aliphatic amine
$(CH_2O)_x$/DMSO	DMSO/methylamine
CCl_3COH/dipolar aprotic liquid	N-Methylmorpholine-N-oxide dimethylacetamide/LiCl

TABLE 2.   Activating Pretreatments for Cellulose
Prior to Dissolution in Nonaqueous Solvents

Preswelling in H_2O with subsequent solvent exchange
Decrystallization with liquid NH_3
Reduction in *DP* by acid hydrolysis
Mechanical desintegration

and 2) the minimal concentration of the active component necessary for complete
dissolution depends largely on the physical structure of the sample, and is consider-
ably lowered by an activating pretreatment (for example, with liquid ammonia).

The dilute solution viscosity of cellulose in many nonaqueous solvent systems
is rather high as compared to conventional aqueous ones due to the high viscosity
of the solvent itself and sometimes the chain-stiffening effect of complex formation
between cellulose and solvent. A steep viscosity increase is observed with increasing
cellulose concentration [3]. The steepness of the η vs c curve can be reduced in
special cases by changing the solvent composition. At a high cellulose concentration,
a change in the course of η vs c may occur, for example, in a cellulose melt solution
in $NMMNO \cdot H_2O$ due to the formation of a liquid crystalline system resulting in a
viscosity drop.

COMMENTS ON THE MECHANISM OF SOLVENT ACTION

For the derivatizing solvent systems described so far, the chemical reactions
occurring between cellulose and the active agent are rather clearly known today (see
Table 3). Open chemical problems in connection with derivatizing solvent systems
still exist regarding possible side-reactions between the active agent (for example,
an acylchloride) and the solvent acting as the reaction medium and solvating the
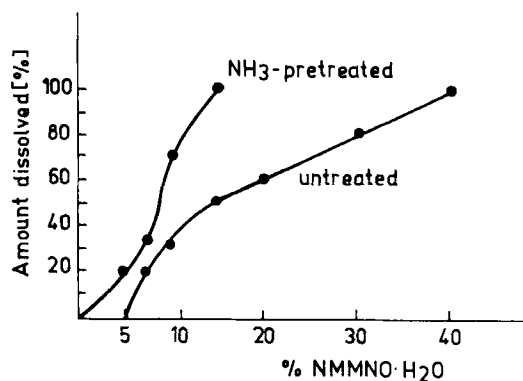unstable cellulose derivative. Thus, the proper choice of this solvent medium and

FIG. 2.   Solubility of a beech sulfite pulp in systems of $NMMNO \cdot H_2O$ and DMSO
before and after activation with liquid NH_3.

TABLE 3. Chemical Reactions in Some Derivatizing Solvent Systems

Cell—OH + N_2O_4	→	Cell—O—NO + HNO_3 Cellulose nitrite
Cell—OH + $(CH_3)_3SiCl$	→	Cell—O—Si$(CH_3)_3$ + HCl Trimethylsilyl cellulose
Cell—OH + CH_2O	→	Cell—O—CH_2—OH Hydroxymethyl cellulose
Cell—OH + CCl_3COH	→	Cell—O—CH(OH)—CCl_3 Cellulose acetate of chloral
Cell—OH + H_2N—CO—NH_2	→	Cell—O—CO—NH_2 + NH_3 Cellulose carbamate
Solid-state reaction		Soluble in aqueous NaOH

especially the limitation of its water content to a sufficient low level are important for securing a smooth and well-defined course of dissolution. DMF, DMSO, and dimethylacetamide are well suited for many of the systems in question. With the silyl system, the choice depends on the DS set by the reaction conditions (Table 4, [4]). Furthermore, a rather complex reaction scheme can be encountered in the decomposing step of the unstable derivative to regenerated cellulose (considered in detail for the nitrite system in Ref. 5). The complexity of this regeneration process is comparable to that of viscose decomposition in fiber formation and can be decisive in judging the technical feasibility of a derivatizing system, as experienced for the N_2O_4/DMF system during the 1970s.

With nonderivatizing solvent systems, polymer–solvent interaction is less clearly and less completely understood than with derivatizing ones, and no generalizable theory is available for guiding the search for new systems. This situation is caused on the one hand by the well-known analytical problems of acquiring quantitative data on intermolecular polymer–solvent interactions, and on the other hand by the fact that enthalpic, entropic, and steric factors contribute to a different extent and by means of different intermolecular forces to the separation of polymer chains in the native fiber structure and their subsequent solvation.

TABLE 4. Solubility of Trimethylsilyl Cellulose
(according to Stein [4])

Liquid	DS_{Si} range of solubility
Ethanol	0.2–0.7
Acetone	1.6–1.8
DMF	0.9–1.7
DMSO	0.3–1.2
Tetrahydrofuran	1.7–3.0
Hexane	2.5–3.0

$$\text{Cell} - \underset{(-)}{O} - \underset{(+)}{H} \ldots\ldots\ldots \underset{(-)}{O} \leftarrow \underset{(+)}{N} \underset{\diagdown R_3}{\overset{\diagup R_1}{-R_2}}$$
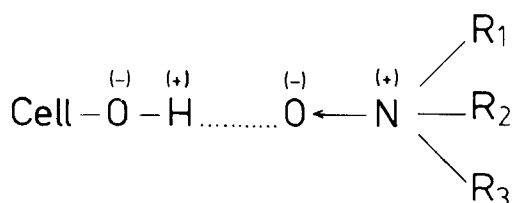
FIG. 3.   Scheme of a cryptoionic H-bond complex of cellulose with an aminoxide.

Nevertheless, some theoretical considerations on the mode of action of nonde-rivatizing cellulose solvents have been published during the last two decades. In stressing the amphoteric nature of the OH-function, Turbak [6] proposed an acid-base theory of interaction between cellulose and aqueous as well as nonaqueous solvents. Nakao [7] and later Schleicher and Philipp [8] considered EDA complex formation to be the dominating mode of cellulose–nonaqueous solvent interaction into which the H as well as the O atom of an OH-function can be involved with different functional groups or different components of the solvent system.

Especially for dipolar aprotic systems like $NMMNO \cdot H_2O$ or dimethylacet-amide/LiCl, Berger and Philipp assumed the formation of cryptoionic H-bond com-plexes according to the scheme given in Fig. 3. These authors also accentuated the dominant role of the OH-group in the C-6 position of the anhydroglucose ring in this complex formation, showing that, for example, a xylan, where the primary $-CH_2OH$ group is missing, does not dissolve at all in this class of organic solvents. Concerning the detailed structure of the complexes formed between cellulose and dipolar aprotic solvent systems containing LiCl as one active compound, different models have been proposed by different authors, as demonstrated in Fig. 4 for the cellulose/dimethylacetamide/LiCl system. A final decision based on the compre-hensive experimental data [9] has not been possible up to now.
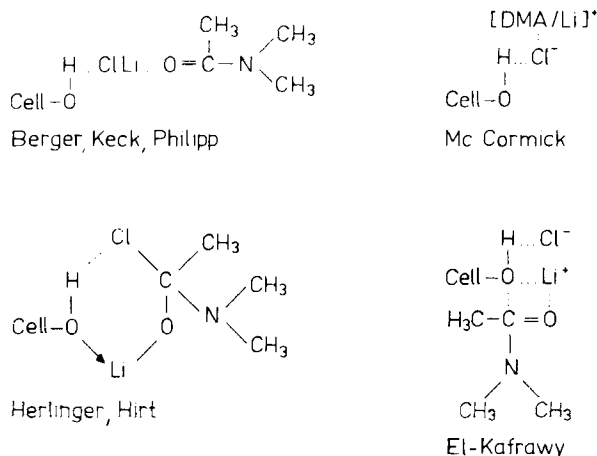
FIG. 4.   Structural models of complexes formed in the system cellulose/dimethylacet-amide/LiCl.

The relevance of steric factors in complex formation between cellulose and nonderivatizing solvents was stressed by several authors, as for example by Isogai et al. [10] in connection with SO_2/aliphatic amine systems, which may be considered as borderline cases between nonderivatizing and derivatizing systems. According to these authors, the different steric conformation of the $-CH_2OH$ group in native and in regenerated cellulose is the main reason for the insolubility of cellulose II in contrast to cellulose I which is easily soluble in an SO_2/amine system.

A discussion of the action of nonderivatizing solvents requires a brief comment on the role of the excess component in binary, ternary, or quaternary systems. This compound, usually a dipolar aprotic liquid like DMF or DMSO, can act as a necessary constituent of the active solvent complex, as for example in the methylamine/DMSO system, securing an optimal solvent power at a definite component ratio. It can further act as an interferring agent in complex formation, for example by dipole forces, and it can finally act just as a diluent for the active component, as in the binary system $NMMNO \cdot H_2O$/DMF.

Besides the chemistry so far discussed, the course of morphological changes of the cellulose fibers during their dissolution in a derivatizing or nonderivatizing solvent has to be considered, and it differs rather widely in dependence on the systems employed. In the N_2O_4/DMF system, for example, spundle-like fiber fragments can be observed, indicating a disintegration of the fiber structure starting from the surface. In the dimethylacetamide/LiCl system, on the other hand, an oblique fiber fracture was observed while assessing the course of dissolution of native cellulose fibers morphometrically [11]. WAXS investigations and level-off DP measurements [12] of fiber residues subsequent to treatment with $NMMNO \cdot H_2O$/DMSO mixtures of stepwise increasing "solvent power" led to the assumption of a "wedge-like penetration" of the solvent into the ordered regions of the fiber structures prior to a complete separation of the polymer chain [13]. According to this concept, enthalpic effects alone between cellulose and dipolar aprotic, nonderivatizing solvents are not sufficient to break the H-bonds in the ordered regions of native cellulose, but must be aided by entropic contributions to achieve dissolution.

FIBER SPINNING FROM NEW SOLVENTS

Parallel to scientific investigations on the peculiarities of cellulose solid-state structure formation from nonaqueous solutions, strong efforts were made during the last two decades to develop spinning processes based on the new cellulose solvents. As demonstrated by a large number of patents and publications during the last 20 years, threads with good textile properties obviously can be spun from numerous solvent systems. This holds true for derivatizing as well as for nonderivatizing systems.

But as recognized rather early, fair thread properties are a necessary but not a sufficient prerequisite for the success of a new man-made fiber technology. The toxicology of the compounds involved, the feasibility of recycling of the chemicals, and, of course, the economy of the whole process are decisive criteria of selection for the numerous approaches primarily considered. Problems of recycling the chemicals and of process ecology have proved to be a serious handicap, especially with

regard to some derivatizing nonaqueous systems like N_2O_4/DMF. Nonderivatizing solvent systems were therefore definitely favored during the last 10 years.

Aminoxides, especially NMMNO, are considered today as the most promising nonaqueous cellulose solvents for establishing new processes of man-made fiber spinning. According to present knowledge, the reagent is nontoxic. Problems of spontaneous decomposition and of recovery from an aqueous spinning bath seem to be solved, as reported recently in Ref. 14 where a sorption of the basic NMMNO on a cation-exchange resin was employed for recovery. As demonstrated by the data in Table 5 (summarized from Refs. 15 and 16), aminoxide-spun threads are now superior to normal grade viscose rayon or staple and can successfully compete with cotton or even polyester in several areas of application.

A pronounced tendency to fibrillate and a too low extension at break obviously are widely overcome now by optimizing the interaction between orientation and relaxation of the polymer chain during the process of fiber structure formation. According to Chanzy [17], a variation of mechanical fiber properties in a rather broad range could be realized by suitable additives (inorganic salts) to the spinning solution. These technological achievements are backed by fundamental studies on supermolecular structure and morphology of the threads obtained in comparison to fibers spun by conventional or other new solvent processes. Recent studies on fiber morphology by Chanzy [17] and on crystallite and fibril dimensions by Schurz and Lenz [18] may be explicitly mentioned here.

Cuculo described [19] a wet-spinning process of cellulose dissolved in the system NH_3/NH_4SCN employing aliphatic alcohols for coagulation, and he also gave in this publication a comprehensive report on the structure and properties of the fibers obtained. Tenacities up to 160 mN/tex and an elongation up to 11% were measured with these fiber samples. The same author reported on the properties of tough, clear cellulose films from a liquid crystalline cellulose/NH_3/NH_4SCN system [20].

The system dimethylacetamide/LiCl yields threads of a different physical structure, but also of acceptable textile properties [21]. It recently received addi-

TABLE 5.   Textile-Mechanical Data of Aminoxide-Spun Fibers in Comparison to Conventional Ones

Fiber type	Ref.	Tenacity, cN/tex			Elongation, %		Wet modulus, 5% ext.	Water regain, %
		Dry	Wet	Loop	Dry	Wet		
Aminoxide	15	45	39	19	12	—	—	—
spun	16	40–42	34–38		13–15	16–18	270	11.5
Viscose	15	26	14	7	17	—	—	—
rayon staple	16	20–26	10–15		20–25	25–30	50	13
Cotton	15	34	41	21	8	—	—	—
	16	20–24	26–28		7–9	12–14	100	8
Polyester	15	—	—	—	—	—	—	—
staple	16	55–60	54–58		25–30	25–30	210	0.5

tional interest as a solvent system for spinning fibers of polymer blends, e.g., of cellulose with synthetic fiber-forming polymers. As shown by Berger et al. [22], clear solutions containing cellulose and polyacrylonitrile can be obtained in different ways and with a sufficiently high "kinetic stability" to perform without previous phase separation in a wet-spinning process. Fibers containing 5% cellulose had significantly higher water sorption compared to the original synthetic material, but a considerable drop in fiber tenacity has still to be taken into account. This is just an example of the variety of threads spun from cellulose/synthetic polymer blends obtained in nonaqueous solvent systems ([24] and Table 6). Doubtless this research topic is of current interest for obtaining new speciality fibers from commercially available polymers, but the technical feasibility of this approach and the ultimate fiber properties obtainable by it are still open questions. Furthermore, the moderately fast but finally complete biodegradability of cellulose threads, which may be an asset of these materials, especially in the future, is ruled out totally or partially by turning to cellulose/synthetic blends within a single fiber, and these materials can be expected to behave rather like synthetics.

So far, this contribution has been concerned with nonaqueous cellulose solvent systems only, and at present this is also today's main route to new processes for the manufacture of man-made fibers. But it cannot be neglected that new approaches in the area of aqueous solvent systems for cellulose have also become visible in recent years. Besides attempts in the 1970s to revive the cuprammonium process, the route via cellulose carbamate must be mentioned. As reported in numerous publications and patents, and quite recently in Ref. 23, cellulose can react with urea at a temperature above 150°C to an alkali-soluble cellulose carbamate which is subsequently decomposed to cellulose, CO_2, and NH_3 or the corresponding ions, depending on the pH. Besides good mechanical fiber properties, ecological compatibility and the feasible use of existing viscose plant equipment are claimed as advantages of this new process based on an aqueous derivatizing system.

HOMOGENEOUS CELLULOSE DERIVATIZATION IN NONAQUEOUS SOLVENT SYSTEMS

Besides the development of new spinning technologies for man-made fibers as the main route of potential application, the new nonaqueous solvents have deci-

TABLE 6.   Blends of Cellulose with Synthetic Polymers Spun from Nonaqueous and Aqueous Solvent Systems (according to Berger [22])

Blended polymers	Solvent system
Cellulose/polyamidimid	CH_2O/DMSO
Cellulose/polyacrylonitrile	CH_2O/DMSO
	N_2O_4/DMF
	LiCl/dimethylacetamide
Cellulose/polymethyl methacrylate	$(Et_4N)Cl$/DMSO
Cellulose/acrylonitrile copolymer	$ZnCl_2$ in water

TABLE 7.   Regioselectivity in Sulfation of Cellulose Trinitrite

| Sulfating agent | Conditions of reaction | | | Total DS by NMR | Partial DS by NMR | | | |
	Mol agent / Mol AGU	Time, h	Temper- ature, °C		C-2	C-3	C-6	% C-2
NOSO$_4$H	2	4	20	0.35	0.04	—	0.31	11
H$_2$NSO$_3$H	2	3	20	0.40	0.10	—	0.30	25
SO$_2$Cl$_2$	2	2	20	1.00	0.30	—	0.70	30
SO$_3$	2	3	20	0.92	0.26	—	0.66	28
	2	1.5	−20	0.55	0.45	—	0.10	82
	4	3	−20	0.99	0.56	0.16	0.27	56

sively broadened the scope of the organic chemistry of cellulose, making possible an acylation or alkylation of the original polymer in a homogeneous system at aprotic conditions. Derivatizing as well as nonderivatizing solvent systems have been successfully employed for this purpose [24]. Because a survey of the reaction and of the problems arising in product isolation and purification exceeds the frame of this contribution, only one topic shall be discussed here briefly, i.e., the route opened by the new solvents to a regioselective substitution in the C-2, C-3, and C-6 positions of the anhydroglucose ring. Besides its scientific relevance, this regioselectivity of partially substituted cellulose derivatives can influence product properties; for example, the biological activity or the rheological behavior in solution. According to our current experience, derivatizing systems with their well-defined state of chemical binding are generally more promising here than are nonderivatizing ones.

As shown by us recently, the action of the N$_2$O$_4$/DMF system can be regulated to obtain a homogeneous solution of a completely substituted cellulose trinitrite. Subsequent sulfation by transesterification of the very instable nitrite ester group can be regulated in its regioselectivity via the reactivity of the nitrite group in the C-2, C-3, and C-6 positions, depending on the sulfating agent and on the reaction temperature [25, 26]. After decomposition of residual nitrite groups in a protic medium, stable, water-soluble, low to medium DS cellulose sulfate half-esters are obtained with a distribution of substituents adjustable via the reaction conditions (Table 7).

CONCLUDING REMARKS

In finalizing this survey on composition, way of action, and promising applications of nonaqueous solvents for cellulose, two comments of a more general nature seems to be justified. Beyond its scope of informing on recent experimental results and theoretical model consideration, this contribution intended to visualize the integrative character of the research area covered here in promoting a necessary cooperation and integration between cellulose chemistry and general polymer science.

Despite the ample knowledge so far acquired, research on the new cellulose solvents and especially on their future applications is still a very dynamic development. Alternative and sometimes competitive routes have to be further pursued before a comprehensive decision is possible. This will involve the advantages and shortcomings of derivatizing in comparison to nonderivatizing solvents as well as the competition between nonaqueous and aqueous systems in man-made fiber manufacture. Moreover, there is some connection to the more general question on the future share of natural polymers in the total production of polymer materials and functional polymers in a forthcoming period of time, where besides a safe and profitable technology of polymer synthesis and processing and adequate end-use properties, recycling, chemical re-use, and/or ecologically safe disposal will also be a decisive criterion.

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