Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polymer 44 (2003) 4117–4126
polymer
www.elsevier.com/locate/polymer

Cellulose in lithium chloride/*N*, *N*-dimethylacetamide, optimisation of a dissolution method using paper substrates and stability of the solutions

Anne-Laurence Dupont*

CNRS, umr 8573, Centre de Recherches sur la Conservation des Documents Graphiques, 36 rue Geoffroy-Saint-Hilaire, 75005 Paris, France

Received 22 January 2003; received in revised form 25 April 2003; accepted 15 May 2003

Abstract

Activation and dissolution in lithium chloride/*N*, *N*-dimethylacetamide (LiCl/DMAc) of cellulose from paper substrates are studied. The importance of the multiple parameters involved such as salt concentration, sample source and preparation is shown in a literature review. The experiments are carried out in order to perfect the method of activation and dissolution of paper containing different kinds of additives, typically found in historic papers. The suitability and efficiency obtained in the different trials are evaluated. The final procedure involves the activation by solvent exchange, with a water/methanol/DMAc sequence, followed by dissolution in 8% LiCl/DMAc at 4 °C. A study of the stability of the cellulose solutions in the experimental conditions showed that no degradation nor aggregation occurred during the solvation process and even after several months and confirmed the non-aggressiveness of LiCl/DMAc.

Keywords: Paper; Cellulose; Lithium chloride/*N*, *N*-dimethylacetamide

1. Introduction

Research into new solvent systems for non-water soluble polysaccharides, such as cellulose, is an area of constant development mostly because of the significant economical impact these polymers have in the pharmaceutical, food, paper and textile industry. In that respect, it is important to study the solution properties of polysaccharides in order to determine their structure and molar mass distribution (MMD), predict their behaviour during processes, and optimise their functions as end products. In recent years, lithium chloride/*N*, *N*-dimethylacetamide (LiCl/DMAc) has become very popular. It was first discovered to dissolve polyamides and chitin in 1972 [1–5]. Its use quickly spread, and the application to dissolve cellulose was done for the first time almost concomitantly by McCormick [6] and Turbak [7]. These early studies, as well as a review article by Dawsey and Mc Cormick [8], showed the uniqueness of LiCl/DMAc as solvent system. The methods initially proposed were rapidly adapted to suit the cellulose source and the sample characteristics in numerous applications.

The popularity of LiCl/DMAc is linked to the clear advantage that a direct dissolution method has over derivatisation by being faster, easier and more reproducible. But the major advantage of LiCl/DMAc lies in the fact that it can be used as mobile phase in size-exclusion chromatography (SEC) with the column packings such as poly(styrene-divinyl benzene) (PSDVB). The solvent and mobile phase being identical simplifies the procedure. SEC of cellulose in LiCl/DMAc was carried out for the first time by Ekmanis [9,10].

After two decades of use, a generally accepted mechanism still remains to be revealed in order to fully explain the solvation of cellulose in LiCl/DMAc, in particular the solvent–lithium interaction and the crucial role of the chloride ion. Slightly different interpretations are given by McCormick et al. [11], El-Kafrawy [12], Turbak [13], and Morgenstern et al. [14], but all emphasise as basic principle that the lithium ions are tightly linked with the carbonyl group of DMAc while the chloride ions are left unencumbered. Thereby Cl^- is highly active as nucleophilic base and plays a major role by breaking up the inter- and intra-hydrogen bonds. Some authors attribute to Cl^- the ability to complex the three hydroxyl groups of the anhydroglucose unit by hydrogen bonding, while the counterpart of the solvent complex, the $[Li\ DMAc]^+$ macro-cation, is believed to be more loosely bound [11].

* Corresponding author. Tel.: +33-1-4408-6992; fax: +33-1-4707-6295.
E-mail address: aldupont@mnhn.fr (A.L. Dupont).

0032-3861/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00398-7

More recently, it has been proposed that cellulose takes part in the coordination sphere of Li^+, this being one of the driving forces in the dissolution of the polymer [15].

2. Literature review and aim of the study

Prior to dissolution, the activation step is crucial for opening up the polymer chains into the most relaxed conformation, in order to enhance the diffusion kinetics of the solvent to the tightly packed crystalline regions that are less accessible. For most of the polymers, this means mainly allowing sufficient time for chains to unfold. The larger the molar mass (M_r) and crystallinity are, the longer is the time needed to obtain a true solution. The most effective activation methods described in the literature [6–8] are the polar medium swelling (usually with water followed by DMAc at room temperature), and the activation with hot DMAc. First, water swells and opens the structure; inter- and intra-molecular hydrogen links are replaced by hydrogen links with H_2O. DMAc introduced subsequently impedes the inter- and intra-hydrogen bonds to re-form. The necessity of allowing enough time for a good desorption of the water from the more crystalline regions of the cellulose in the solvents used in the subsequent steps for an optimal activation is paramount [16]. Heat activation, as first proposed by Ekmanis [9,10], is based upon the fact that at or near its boiling point, the amide has sufficiently high vapour pressure to penetrate in the fibre and swell it. DMAc refluxes with the cellulose at a temperature close to the solvent boiling point [17,18]. Heat activation is reported by some authors as more advantageous than polar medium activation because it requires less LiCl in the subsequent dissolution phase, but foremost because it is a one-step procedure thus allowing easier handling of a large number of samples [19]. Turbak found that recovered cellulose from heat-activated solutions had lost 10% in intrinsic viscosity, which the author considered as a non-significant degradation [7]. Dawsey and McCormick [8], and Terbojevich et al. [20] observed that the solutions prepared via heat activation were slightly coloured, which they attributed to oxidative degradation of the polymer at high temperature. They found that flushing nitrogen in the solutions minimised this oxidation and resulted in clear solutions. More recently Potthast et al. [21] showed that cellulose underwent depolymerisation upon prolonged periods in heated 9% LiCl/DMAc. This degradation increased with the temperature and the time, and was more or less pronounced depending on the pulp type. The authors found that this degradation occurred via endwise peeling reactions due to *N*,*N*-dimethylacetoacetamide, a condensation product of DMAc formed during heating, and via random cleavage due to *N*,*N*-dimethylketeniminium ions that form at temperatures above 80 °C. The latter are extremely reactive electrophilic ions able to cleave glycosidic bonds.

The thorough literature review by Dawsey and McCormick [8] of the experimental conditions tested by different authors showed that the relative proportions of LiCl and cellulose were critical for optimal dissolution. 'Ideal' concentrations of LiCl by weight of cellulose were reported within as wide a range as 2 to 12% [6,7]. For cotton fibres [18,19] and for a vast variety of wood fibres such as softwood and hardwood in Kraft pulps [18], 8% LiCl was found the least amount necessary to achieve complete dissolution. However, using heat activation, even high-M_r cotton celluloses appeared to completely dissolve at lower LiCl concentrations [19,22]. According to McCormick et al. [11], a critical number of complexed sites seems to be required, and concentrations greater than 6% LiCl are necessary for a complete dissolution of low-M_r celluloses. Reportedly, at LiCl concentration above 12% [18] to above 15% [7], the DMAc becomes supersaturated with the salt and the cellulose tends to precipitate out of solution. Interestingly, in a recent publication Potthast et al. [23] determined the limiting soluble concentration of LiCl in absolutely dry DMAc to 8.46%, thus pointing to the need of re-evaluating former data in the literature taking into account the water content in the solvent.

Aggregate free solutions of polymers are in general difficult to prepare [24]. Sjöholm et al. [25] found the concentration of LiCl critical in the formation of aggregates upon dissolution of woodpulp and cotton linter, independently of the sample concentration. For hardwood Kraft pulp, the proportion of aggregates increased when the concentration of LiCl increased from 6 to 8% and from 8 to 10%. Strlič et al. [26] recently reported the important role of LiCl concentration regarding the accuracy of the M_r determined. After dissolution of cellulose in 8% LiCl/DMAc, and further dilution for SEC analysis, a sample containing 3% LiCl showed lower M_r than a similar sample containing only 1% LiCl. The authors attributed this to a decrease in the intermolecular interactions and extent of aggregation during sample preparation thereby pointing sample preparation prior to injection as a decisive process. Other studies reported the presence of aggregates under specific conditions [20]. Röder et al. showed that aggregates and associates of cellulose from diverse sources (microcrystalline cellulose and cellulose from softwood Kraft pulp and hardwood sulphite pulp) forming in 6 and 9% LiCl/DMAc could be disintegrated upon dilution to 2.6% LiCl (i.e. SEC concentration) [27], but only within certain limits of cellulose versus salt proportion. In a solution with too low LiCl concentration and/or too high cellulose concentration, the solvent was unable to completely rupture the strong hydrogen bonds in the cellulose [28]. The crucial role of trace amounts of water in LiCl/DMAc in promoting the formation of cellulose aggregates in solution was recently demonstrated [23], which evidenced the so far neglected role of water in the solvent system LiCl/DMAc.

Other parameters in the dissolution process such as the cellulose concentration as well as the supramolecular structure of the polymer (which depends on the cellulose

source), its molar mass [29], and the sample preparation for the activation step greatly influence the dissolution process. McCormick [6] reported that solutions of 1 to 5% cellulose powder could be achieved in less than one hour, while it took 24 to 48 h for solutions of 6 to 15% cellulose. Turbak [13] noted that upon activation by water swelling and solvent exchange, up to 12–15% cellulose of relatively low-M_r (9×10^4 g mol^{-1}) could be dissolved in 10% LiCl/DMAc in 4–6 h. However, with higher M_r (3×10^5 g mol^{-1}), solutions of up to about 4% cellulose only could be prepared. Ekmanis [9] also noted that the higher the M_r, the more difficult is the dissolution. According to Silva and Laver [18], among solutions ranging from 0.8 to 1.6% cellulose (wt/v) the concentration resulting in ideal dissolution was 1.2%. Similarly, Timpa [19] found the ideal cellulose concentration also being 1.2%. While most of the early studies focussed on concentrated solutions of low-M_r cellulose, Striegel and Timpa chose to study the dissolution and characterisation of high-M_r cellulose [22]. For Kennedy et al. [30] the maximum concentration of cotton cellulose for complete dissolution in 10% LiCl/DMAc was 0.075%, compared to 0.15% for softwood and hardwood cellulose. The authors suggested this was due to higher crystallinity of cotton cellulose, and to the difference in composition and processing of the pulps. This referred especially to the treatment used to remove lignin in wood pulps, which creates voids and a wide distribution of pores. Such a microporous structure eases the penetration of activation liquids and solvent.

Using polar medium activation, sulphite pulp samples were reported to dissolve faster than cotton linter [31]. Again, this was attributed to the high crystallinity of cotton cellulose. Depending on the cellulose source and pulping process (pulp from softwood, hardwood, Kraft, sulphite, bleached or unbleached), the necessary time required for the different steps of activation and dissolution in order to achieve clear solutions varied widely [18]. Here also, longer times were attributed to higher M_r, crystallinity, and α-cellulose contents. Despite these observations, inconsistencies remain about the role of crystallinity in the solubilisation process. For instance, hardwood Kraft pulp (low crystallinity) dissolves much more slowly than cotton (high crystallinity) [18]. Recent publications also confirm that the degree of crystallinity is not responsible for the difference in solubility between cellulose substrates [32].

The solutions of cellulose in LiCl/DMAc are reported to be extremely stable [33]. Some researchers found no degradation of the polymer after several months in solution [20] and even years at room temperature [7,34]. High LiCl concentrations (above 10%) were reported to have no degradation effect on cellulose over time [30]. McCormick et al. [11] noted a slight decrease of 2% in relative viscosity of cellulose solutions in 9% LiCl/DMAc over 30 days, which they attributed to changes in inter- and intra-molecular hydrogen bonding. Strlič et al. [35] showed that cellulose from linters powder that was submitted to an oxidation treatment, in order to increase the sensitivity to solvent-induced degradation, and analysed immediately after the dissolution did not undergo further degradation in 8% LiCl/DMAc. In a more recent study [26], the authors found that the cellulose in 1% LiCl/DMAc at room temperature exhibited a decrease in M_n of 47 g mol^{-1} per day. For a mid-M_r cellulose of 3×10^5 g mol^{-1} this would correspond to a negligible decrease after 30 days of 0.5% of M_n.

In contrast, Jerosch [36] found LiCl/DMAc had some degrading action on cellulose in specific cases. When cellulose solutions were kept in 8% LiCl/DMAc at 40 °C over 5 days, M_r was stable for 2 weeks but decreased by 23% after 22 days. The initial degradation state of cellulose and the temperature–time history was found paramount in the stability of cellulose solutions. However, with cotton linters from paper, when dissolution and storage were carried out at 4 °C, no decrease in M_r was found for up to 2 weeks. With papers subjected to accelerated aging, either heat/humidity or pollution, even at low temperature, M_r started dropping slightly after one week.

This literature overview shows that there is no real agreement neither as to which activation mechanism nor as to which dissolution procedure are best or even adequate, as numerous parameters play a role. Nevertheless, it is noteworthy that the majority of these studies were carried out using cellulose from pulp provenience. In the present study, the goal was to establish a non-degradative and reproducible method of dissolution to be used with historic papers for their subsequent analysis and characterisation by SEC. Therefore paper was used as source of cellulose. Since historic papers from the 14th to the 18th century were usually made from rags (cotton or linen) and various kinds of additives were used for sizing[1] these papers, the model chosen for this study was pure cellulose paper to which common historically used compounds were added. These consisted mainly of gelatine and/or alum (aluminium potassium sulphate). The prepared papers were artificially aged, and the dissolution was tested on unaged and aged papers. The two activation methods described above, namely heat activation and solvent exchange activation, as well as different dissolution parameters were investigated in order to establish an optimal method to dissolve the unaged or aged prepared papers in LiCl/DMAc. The evaluation of the degree of dissolution was made by visual examination.

[1] The modern definition of sizing refers to the treatment of paper carried out in order to achieve resistance to the sorption of liquid, either by means of additives incorporated in the papermaking furnish (internal sizing) or by surface application to a formed and dried paper (surface sizing). The historical definition refers to a hybrid form of surface sizing, as it was done after the sheet formation but involved an immersion process, and as such, achieved a total penetration of the size in the paper web.

Table 1
High temperature activation and dissolution experiments

No.	Sample	Activation	LiCl concentration	Dissolution time and efficiency	Yellowing
1a	W[a] unsized unaged, RC[b]	1 h DMAc 150 °C	(1) 5%, 100 °C, 3 days (2) After 3 days, added to 10%, 100 °C	(1) 3 days, no dissolution (2) 5 days, mostly dissolved	−[c] −
1b	W/A5[d] aged 4 days, RC	1 h DMAc 150 °C	(1) 5%, 100 °C, 3 days (2) After 3 days, added to 10%, 100 °C	(1) 3 days, no dissolution (2) 11 days, mostly diss., crystalline deposit	+[c]
1c	W/A5 aged 13 days, RC	1 h DMAc 150 °C	(1) 5%, 100 °C, 3 days (2) After 3 days, added to 10%, 100 °C	(1) 3 days, no dissolution (2) 11 days, mostly diss., crystalline deposit	+
2	W unsized unaged, RC	22 h DMAc 150 °C	(1) 8%, 100 °C, 6 days (2) After 6 days, added to 12%, 100 °C	(1) 6 days, no dissolution (2) 9 days, little dissolved	+ +
3	W unsized unaged, RC	1 h DMAc 150 °C	10%, 100 °C	5 days, mostly dissolved	+/−
4	W/K12.5[e], RC	1 h DMAc 150 °C	13%, 100 °C	8 days, mostly diss., gelatine precipitated	++
5a	W unsized unaged, C[f]	1 h DMAc 150 °C	(1) 8%, 100 °C (2) T° immediately lowered to 50 °C	3 days, mostly dissolved	−
5b	W unsized aged 91 days, C	1 h DMAc 150 °C	(1) 8%, 100 °C (2) T ↓ 50 °C	3 days, mostly dissolved	−
5c	W/K0.5[g] aged 91days, C	1 h DMAc 150 °C	(1) 8%, 100 °C (2) T ↓ 50 °C	3 days, mostly dissolved	−
6a	W unsized unaged, C	1 h DMAc 150 °C	(1) 12%, 100 °C (2) T ↓ 50 °C	(1) 3 days, partly dissolved (2) no further dissolution with ↑ time	−
6b	W unsized unaged, RC	1 h DMAc 150 °C	(1) 12%, 100 °C (2) T ↓ 50 °C	(1) 3 days, partly dissolved (2) no further dissolution with ↑ time	−
7a	W unsized unaged, C	1 h DMAc 150 °C	(1) 5%, 100 °C (2) T ↓ 50 °C	11 days, partly dissolved	−
7a′	W unsized unaged, C	1 h DMAc 150 °C	(1) 8%, 100 °C (2) T ↓ 50 °C	11 days, partly dissolved	−
7b	W unsized unaged, dry[h]	1 h DMAc 150 °C	(1) 5%, 100 °C (2) T ↓ 50 °C	11 days, partly dissolved	−
7b′	W unsized unaged, dry	1 h DMAc 150 °C	(1) 8%, 100 °C (2) T ↓ 50 °C	11 days, partly dissolved	−
8a	W/N0.5[i] aged 91 days, C	1 h DMAc 150 °C	(1) 10%, 100 °C (2) T ↓ 50 °C	4 days, little dissolved, no further dissol.	−
8b	W/N2[i] aged 91 days, C	1 h DMAc 150 °C	(1) 10%, 100 °C (2) T ↓ 50 °C	4 days, little dissolved, no further dissol.	−
8c	W/K0.5[i] aged 91 days, C	1 h DMAc 150 °C	(1) 10%, 100 °C (2) T ↓ 50 °C	4 days, little dissolved, no further dissol.	−
8d	W/K2[i] aged 91 days, C	1 h DMAc 150 °C	(1) 10%, 100 °C (2) T ↓ 50 °C	4 days, little dissolved, no further dissol.	−

[a] Whatman No.1 paper.
[b] Room environment conditions.
[c] ' − ' = no yellowing; ' + ' = yellowing.
[d] A5 = sample immersed in 5% aqueous alum solution (wt/v).
[e] K12.5 = sample sized with Kind and Knox (K) gelatine 12.5% uptake (wt/wt).
[f] C = conditioned to 23 °C and 50% rH [37].
[g] K0.5 = sample sized with K gelatine, 0.5% uptake (wt/wt).
[h] Sample dried in a desiccator over drierite for 7 days.
[i] N0.5, N2, K0.5 and K2 = samples sized with Norland (N) and K gelatines, 0.5 and 2% uptake (wt/wt).

3. Development of a method for the dissolution of cellulose from paper in LiCl/DMAc

3.1. Experimental

3.1.1. Solvent preparation

Both LiCl and DMAc are very hygroscopic, and water has to be excluded from the solvent system, since its presence hinders complexation with cellulose [7] and promotes the formation of polymer aggregates [23]. Depending on the authors, the maximum amount of water in the final solution should be below 0.2% [23] to below 5% [7].

LiCl was oven-dried and stored in a desiccator over drierite ($CaSO_4$). Aliquots of LiCl were weighted swiftly when needed and placed back in the desiccator until dry before use. From the two DMAc drying methods tested, namely heating at 100–110 °C for 10 min in order to drive off the residual moisture, and adding aluminium sodium silicate molecular sieve (0.4 nm effective pore size) in the solvent bottle, the latter was chosen even though both methods seemed to achieve comparably efficient drying, as it was noted that heating could lead to a yellowing of the DMAc, which was attributed to oxidation. When dry, DMAc was filtered through 0.5 μm pore filters with a

Table 2
Polar medium exchange activation and warm, ambient or cold temperature dissolution experiments

No.	Sample type	Activation phase	Solvent preparation	Dissolution phase	Cellul conc	Dissolution time and efficiency
1	W unsized unaged	(1) 60 min H_2O room T° (2) 30 min MeOH room T° (3) 1 h DMAc room T° (4) 65 h DMAc room T°	LiCl added to DMAc room T°	8% LiCl/DMAc room T°	1%	Dissolution in 48 h
2	W unsized unaged	(1) 30 min H_2O room T° (2) 15 min MeOH room T°,2x (3) 15 min DMAc room T°, 2x	LiCl added to hot DMAc[a]	6.7 % LiCl/DMAc room T°[b]	0.83 %	Dissolution in 9 days
3	W unsized unaged	Same as sample '2'	LiCl added to hot DMAc	6.7 % LiCl/DMAc at 40 °C	0.83 %	Diss. incomplete after 9 days
4a	W unsized unaged	(1) 60 min H_2O 40 °C	LiCl added to cooled DMAc	8 % LiCl/DMAc room T°	1 %	Diss. in less than 48 h both
4b	W unsized aged 94 days	(2) 45 min MeOH room T°,2x (3) 45 min DMAc room T°, 2x				
5a	W/K2[c] unaged	(1) 30 min H_2O 40 °C, 2x	LiCl added to cooled DMAc	8% LiCl/DMAc room T°	1%	Diss. in less than 48 h both
5b	W/K0.5[d] aged 94 days	(2) 45 min MeOH room T°,2x (3) 45 min DMAc room T°, 2x				
6	W unsized unaged	(1) 3 h H_2O 40 °C (2) 15 min MeOH room T°,2x (3) 15 min DMAc room T°, 2x	LiCl added to cooled DMAc	8% LiCl/DMAc room T°	1%	Dissolution in 48 h
7	W unsized unaged	(1) 16 h H_2O 40 °C (2) 15 min MeOH room T°,2x (3) 15 min DMAc room T°, 2x	LiCl added to cooled DMAc	8% LiCl/DMAc room T°	1%	Dissolution in 48 h
8	W unsized unaged	(1) 60 min H_2O 40 °C (2) 45 min MeOH room T°,2x (3) 45 min DMAc room T° (4) 16 h DMAc room T°	LiCl added to dry DMAc[e]	(1) 8% LiCl/DMAc room T° (2) Placed at 4 °C after 16 h	1%	Dissolution in 48 h

[a] DMAc heated to 100–110°C for 10 min to drive off the moisture.
[b] 6.7% LiCl/DMAc achieved by adding 5 ml 8%LiCl/DMAc and 1 ml of DMAc to the cellulose sample.
[c] K2 = sample sized with K gelatine, 2% uptake (wt/wt).
[d] K0.5 = sample sized with K gelatine, 0.5% uptake (wt/wt).
[e] DMAc dried with molecular sieve.

hydrophilised polytetrafluoroethylene membrane (Millex LCR, Millipore). If not used immediately, the solvent was stored under nitrogen at 4 °C until use, usually within the same week.

In the trials of high temperature activation/dissolution, the appropriate amount of LiCl was added directly in the vials containing the activating cellulose in the final volume of DMAc (see Section 3.1.3.1). In the procedure of dissolution following solvent exchange activation, LiCl/DMAc was prepared in stock solution by adding the required amount of dry LiCl to 8% in warm DMAc (40 °C) under magnetic stirring. LiCl dissolved within one hour. Warm DMAc allowed for the best dissolution of the salt over DMAc at room temperature and DMAc heated to 100 °C (Table 1).

3.1.2. Sample preparation

The model paper source was Whatman No.1 filter paper (denoted W). Aqueous solutions of two types of gelatine, a photographic grade type B (Gelita Type 8039, Lot 1, Kind and Knox, Inc.) and a pharmaceutical/food grade type A (High Molecular Weight Gelatin batch No. 7345, Norland products, Inc.), as well as aqueous solutions of alum were prepared in various concentrations for immersing the model papers. Some of these papers were artificially aged as suspended sheets in a climate chamber Versatenn (Tenney Environmental) at 80 °C and 50% relative humidity (rH) for various periods of time ranging for 4 to 94 days.

In paper substrates, the access of the liquids used for activation to the cellulose molecules has to be facilitated. Grinding is necessary in order to reduce surface heterogeneity. Native and chopped or cut fibres have been reported to result in incomplete and inconsistent dissolution [19,37]. This was confirmed in the present research by a trial of heat activation/dissolution of W paper cut in small pieces (2 × 2 mm), which did result in very poor dissolution state compared to paper defibrillated by grinding. To this purpose, a small two-blade blender (50 ml volume capacity) was used where 2 to 2.5 g of paper was ground for five minutes. The samples were placed in a controlled environment chamber at 50% rH, 23 °C [38] to equilibrate for at least 2 days. About 5×10^{-2} g (±0.02%) was weighted for activation/dissolution.

3.1.3. Optimisation of activation and dissolution

The first method tested in order to obtain an appropriate

and efficient dissolution was heat activation/dissolution as proposed by Timpa [19,39], adapted from the 'one-pot' procedure developed by Ekmanis [10]. This procedure was tried in the first place since the activation phase was reported to be faster and less work intensive than the polar medium exchange activation method. The latter procedure, derived from the original method as proposed by McCormick [6] and Turbak [7] was tried secondly. The activation was done in conical bottom 10 ml reacti-vials capped with Teflon lined screw caps, under constant stirring in a heating/stirring unit (Pierce), using V-shaped Teflon-coated magnetic stirrers.

3.1.3.1. High temperature activation and dissolution. Listed in Table 1 are the conditions tested by varying the activation time and the concentration of LiCl. In all the trials, 5 ml of anhydrous DMAc was heated to 150 °C for 10 min, just below boiling temperature (bp = 164–166 °C), in the reacti-vial left uncapped in order to drive residual moisture out. The defibrillated paper sample ($0.05 \pm 1 \times 10^{-5}$ g) was added and the reacti-vial was tightly capped. The activation proceeded at 150 °C with refluxing DMAc.

After activation, the temperature was lowered from 150 to 100 °C and allowed to stabilise for 20 min. Then LiCl was added directly in the reacti-vial. The temperature was either kept at 100 °C or lowered to 50 °C. In the different trials, the amounts of dry LiCl added in the DMAc activation mixture were 5, 8, 10, 12 and 13% (0.25, 0.4, 0.5, 0.6 and 0.7 g in 5 ml DMAc). The sample was left heating/stirring until maximum dissolution was reached, which took from 3 to 4 days. Assuming complete dissolution of the cellulose, the concentration is 10 mg ml^{-1}, i.e. 1% (wt/v).

3.1.3.2. Polar medium exchange activation followed by warm, ambient or low temperature dissolution. Table 2 summarises the experiments of solvent preparation, activation, dissolution time, cellulose concentration and LiCl concentration in order to optimise the efficiency of the dissolution after polar medium activation.

Polar medium activation consisted in a thorough swelling in water followed by exchange first with methanol and second with DMAc. Volumes were 8 to 10 ml and the time and number of exchanges varied in the different trials. An extra step of methanol exchange was added in order to help expel the residual water. By ensuring its total elimination from the paper substrate, a collapse of the fibres and pores structure is avoided, and further penetration of DMAc enhanced. It also ensured optimal dissolution conditions with a dryer sample, as water was recently shown to promote the formation of cellulose aggregates during the dissolution [23].

Two methods were tested for the elimination of the swelling liquid after each of the exchanges: centrifugation and filtration. Centrifugation at 2500 rpm during 20 min was unsatisfactory as the sedimentation was partial and resulted in a non-negligible amount of lost fibres after several centrifugation steps. Filtration under vacuum was found more appropriate, with almost no fibre loss and a satisfactory elimination of the liquids. It was carried out with a glass filter holder (Millipore), using 0.5 μm pore Millex LCR filters (Millipore).

Dissolution took place after filtering out the last DMAc exchange volume, by adding 5 ml of the stock solution 8% LiCl/DMAc to the paper fibres in the reacti-vial. Solutions with lower salt concentration were achieved by diluting this stock solution with anhydrous DMAc. The reacti-vial was tightly capped and left stirring. The different temperatures tested were 40, 20 and 4 °C.

3.2. Results

3.2.1. High temperature activation and dissolution

Table 1 shows the results obtained in the different trials. Complete dissolution could not be achieved in any case. Moreover, the procedure often yielded yellow cellulose solutions. This discolouration was present regardless of the state of degradation (unaged, artificially aged) and composition of the samples (plain Whatman No.1, with/without alum, and with/without gelatine). Long activation time (22 h) was detrimental, resulting in significant yellowing and lack of improved dissolution; one-hour activation was sufficient. Maximum dissolution was reached within 3 to 4 days, and did not proceed further even upon prolonged periods of up to 11 days. The concentration of LiCl appeared critical. The best—yet incomplete—dissolution of paper unsized and unaged, with no yellowing of the solution, was achieved in 3 days with exactly 8% LiCl. This corresponds to a ratio of cellulose to LiCl of 1/8. With less or more LiCl poorer dissolution and/or yellowing were observed.

After activation and upon adding LiCl it was found that if temperature was lowered from 100 to 50 °C, the yellowing could be avoided. This yellowing was believed to arise from degradation of the cellulose in the solvent at high temperature. Indeed, it was expected that prolonged activation times at 150 °C, as well as dissolution at 100 °C in the presence of lithium salts, would most likely degrade the cellulose. This effect was expected to increase in the case of partially oxidised (oxicelluloses) or hydrolysed celluloses such as found in century-old papers. Moreover, at these temperatures, any residual oxygen present in the reacti-vial would contribute to the oxidative degradation of the polysaccharides. This is consistent with the results from Terbojevitch et al. [20], and Potthast et al. [21]. The latter evidenced the formation of furan structures during heat activation in pulps refluxing with DMAc. Due to the action of highly active intermediates formed during the degradation of DMAc with LiCl at temperatures above 80 °C, these chromophores are released from the reducing ends of the cellulose upon cleavage of a glycosidic bond at temperatures above 130 °C [21,40]. Residual moisture present in the paper that would not have been totally

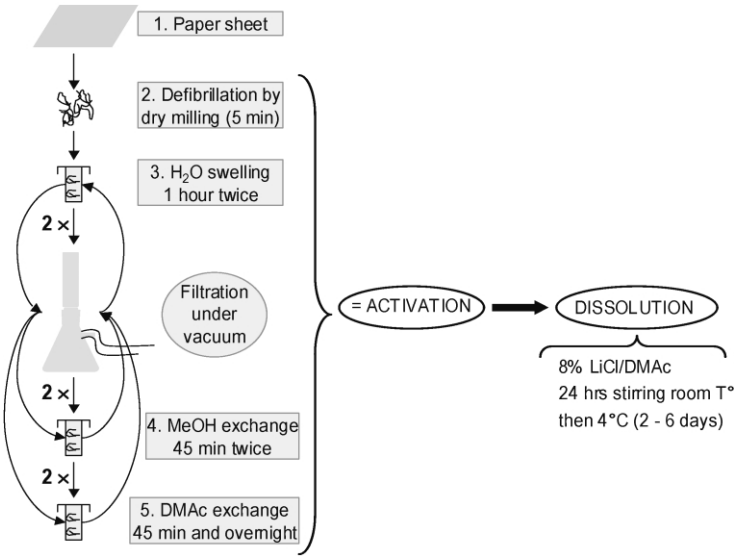

Fig. 1. Schematic representation of the final activation and dissolution procedure for cellulose in LiCl/DMAc.

eliminated after the activation in DMAc could also play a role in the low efficiency of the dissolution [23].

Low gelatine content (0.5% wt/wt) did not hinder dissolution (sample 5c) but with very high gelatine content in the paper (12.5% wt/wt), a precipitation of the gelatine out of solution occurred (sample 4). Visual examination did not allow determining whether the precipitate was gelatine alone or a co-precipitate of gelatine and cellulose. However, it has to be noted that such high gelatine content is seldom found in historic papers.

3.2.2. Polar medium exchange activation followed by warm, ambient or low temperature dissolution

The results reported in Table 2, allowed us to conclude that thorough swelling in water is crucial, and more efficient at 40 °C than at room temperature. Prolonging swelling beyond one hour was found unnecessary. For unsized papers, one water exchange at 40 °C was sufficient, but for sized papers the operation was more efficient if repeated twice. The water helped wash out part of the gelatine, which eased dissolution in the next step. Thorough 'drying' by two consecutive exchanges in methanol and in DMAc of at least 45 min each resulted in faster and more efficient subsequent dissolution.

Complete dissolution could be achieved and was fast, as in most cases it took 48 h and sometimes even less (samples 4a,4b,5a,5b). A concentration of cellulose of 1% (wt/v) was suitable, and LiCl below 8% was not enough for complete dissolution. After initial dissolution at room temperature for 15 to 16 h, completion could be achieved at 4 °C. No yellowing of the solutions occurred in any case.

Thus, water and solvent exchange activation allowed for better subsequent dissolution, and was much less aggressive for cellulose than high temperature activation/dissolution. The procedure could be successfully applied with all kinds of W papers containing gelatine and/or alum in various amounts, unaged and artificially aged. All dissolved totally within 2 to 6 days, depending on the presence or absence of sizing, on the initial gelatine content of the samples, and on the state of degradation (aging). In order to transfer the methodology to real naturally aged papers of different grammage and composition, four cotton and linen rag papers from 17–18th century, and four softwood Kraft pulp papers from the early 20th century (1932), unsized and sized were tested. The latter dissolved very rapidly, in about 30 min. The 17–18th century papers were slower to dissolve, and in one of them, some sparse fibres in suspension were visible still after 14 days [41]. The cause for this difference in the time required for dissolution is likely the type and composition of the papers, as high or low M_r seemed unrelated. The analysis with SEC/MALS/DRI (see Section 4.1) showed that the cellulose in Kraft pulp papers had M_w ranging from 4.7×10^5 to 5.4×10^5 g mol^{-1}, and in 17–18th century papers, M_w ranging from 2.6×10^5 to 6.5×10^5 g mol^{-1} [41]. Even within the latter, the M_r was not related to the dissolution degree.

3.2.3. Final procedure for activation and dissolution of paper

The different steps in the final procedure for activation and dissolution of paper are schematised in Fig. 1. Papers are defibrillated by grinding. Samples of 5×10^{-2} g ($\pm 0.02\%$) are swelled during one hour in 10 ml deionised water at 40 °C (milli-Q, Millipore) twice consecutively. Two exchanges of 45 min each with 8 ml methanol are carried out subsequently, followed by two exchanges with 8 ml anhydrous DMAc (prepared a described in Section 3.1.1). For the latter, 45 min proved enough but for the convenience of a one-day work, the second DMAc

exchange was prolonged overnight. After each exchange, the activation liquids are filtered under vacuum through 0.5 μm pore Millex LCR filters (Millipore). The paper fibres are carefully removed from the filter with tweezers and placed back in the reacti-vial for the next liquid exchange. For each sample, the same filter is kept through the whole procedure in order to minimise fibre loss, to the exception of the heavily sized papers, which tended to clog the filters.

8% LiCl/DMAc is prepared by adding the required amount of dry LiCl in warm anhydrous DMAc (40 °C) (see Section 3.1.1) previously filtered through 0.5 μm pore Millex LCR filters (Millipore). The solvent is freshly made every week and if not used immediately, stored under nitrogen at 4 °C. Dissolution takes place under magnetic stirring after filtering out the second DMAc exchange, by adding 5 ml of 8% LiCl/DMAc to the paper fibres. The sample is stirred at room temperature for 15 h after which the reacti-vial, still capped, is placed at 4 °C to complete dissolution. In all cases, the solutions clear in a reasonable period of time (48 h) with no visible residue or cloudiness, no gel formation, and no yellowing. It was noted that when the sample was not totally dissolved within 7 days, the dissolution did not progress further. Assuming no fibre loss, the concentration of cellulose in the stock sample solution was about 10 mg ml^{-1}, i.e. 1% (wt/v).

Right after dissolution is achieved, the samples are diluted to 0.5% LiCl/DMAc with anhydrous DMAc for analysis with SEC using multiangle light scattering and refractive index detection (SEC/MALS/DRI), i.e. to a sample concentration of about 0.625 mg ml^{-1} (0.0625% wt/v). They are filtered through 0.5 μm Millex LCR filters (Millipore) before injection on the SEC columns. The remaining cellulose solutions are tightly capped and stored at 4 °C, the void headspace of the vial above the solution flushed with nitrogen.

4. Stability of cellulose/LiCl/DMAc solutions

As reported earlier, good stability of cellulose solutions in LiCl/DMAc over time is generally, but not unanimously, reported in the literature. However, fewer mentions could be found of the stability of cellulose/LiCl/DMAc at low temperature [36]. In the present study, it was found important to investigate this stability and the conformational characteristics of the polymer in the solvent, under the experimental conditions chosen.

4.1. Experimental

Two samples of W paper were dissolved in LiCl/DMAc according to the final procedure reported in Section 3.2.3. After completing dissolution, one sample was left in 8% LiCl/DMAc (sample denoted W8-10m) and the second was diluted 1/4 to 2% LiCl/DMAc (sample denoted W2-10m). Both were left standing at 4 °C without nitrogen flushing for a period of 10 months (10m), after which they were diluted to 0.5% LiCl/DMAc for analysis by SEC/MALS/DRI. Each sample was run twice and the values of the molar mass averages (M_r) and scaling factor q were averaged. Three additional samples of W paper dissolved in the same manner were diluted to 0.5% LiCl/DMAc for immediate analysis (W-0m). Each one was analysed in two to three replicates for a total of seven runs, and the values of M_r and q averaged.

HPLC solvent degasser (Degassit™, Metachem Technologies Int.), HP 1100 isocratic pump G1310A (Agilent Technologies), and 7725i manual injector (Rheodyne L.P.) were used. The MALS detector was a Dawn EOS (Wyatt Technologies), and the DRI, an Optilab DSP (Wyatt Technologies). The separation was carried out on a set of 3 poly(styrene-divinylbenzene) (PSDVB) columns 10 μm diameter particles MIXED-B pores, 300 × 7.5 mm (Polymer Laboratories) in series preceded by a guard column 10 μm particles 50 × 7.5 mm (Polymer Laboratories). The system was operated at 60 °C at a flow rate of 1 ml min^{-1} with 0.5% LiCl/DMAc as mobile phase. Injection volume was 100 μl, and run time was 40 min. The data acquisition was carried out with ASTRA software (Wyatt technol.). The dn/dc value of cellulose in 0.5% LiCl/DMAc used was 0.077 ml g^{-1}, as determined by the author [41,42]. RSD% on the mass of cellulose injected calculated by ASTRA for all the papers was 4.2% (uncertainty on the computed values). Each cellulose solution was run two to three times non-consecutively. The values reported are the average of the multiple runs. The SEC/MALS/DRI method used in this experiment is detailed elsewhere [41,43].

4.2. Results

Table 3 reports the average values of M_n, M_w and M_z of W-0m, W2-10m and W8-10m. Their MMD profiles look almost identical (Fig. 2), and only 2.7% difference in the average M_w was found between the 3 samples, which falls within the calculated relative standard deviation (RSD).

Table 3
Average M_r values, polydispersity (PD) and q values of the cellulose samples in fresh and long-standing solutions

	AVG $M_n \times 10^{-5}$ (g mol^{-1})	AVG $M_w \times 10^{-5}$ (g mol^{-1})	AVG $M_z \times 10^{-5}$ (g mol^{-1})	AVG PD	q
W-0m (± RSD %)	3.96 (± 7.8%)	6.68 (± 2.0%)	10.09 (± 4.6%)	1.70 (± 7.1%)	0.59 (± 3.6%)
W2-10m	3.66	6.50	10.29	1.78	0.62
W8-10m	3.51	6.68	10.80	1.91	0.58

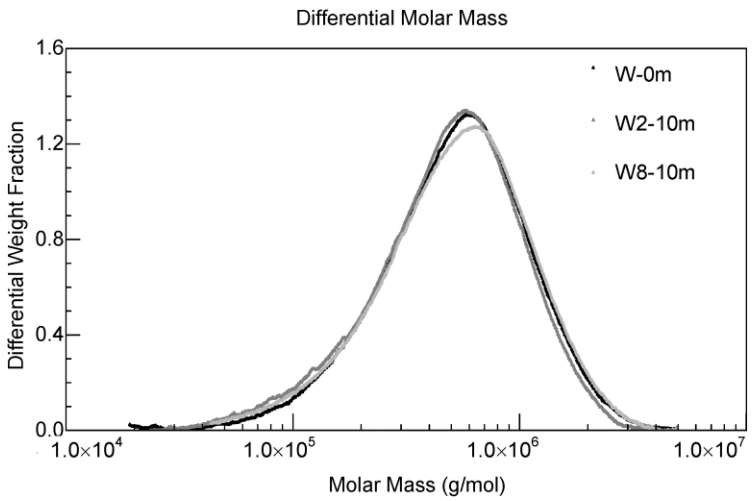

Fig. 2. Overlaid differential molar mass graphs of W-0m, W2-10m and W8-10m.

A slight difference was observed in the value of the polydispersity PD (M_w/M_n). PD was a little larger for the two 10-months old solutions, but while this slight increase falls within the RSD for W2-10m compared to W-0m, it falls just outside the RSD for W8-10m. The broader MMD is due to slightly lower M_n and higher M_z. The somewhat higher proportion of low-M_r and high-M_r fractions in W8-10m may be due to a variation in the hydrogen bonding, and for the high-M_r specifically, to association of the cellulose molecules upon standing at high concentration. In conclusion, despite minute changes occurring over a period of 10 months, the solutions of cellulose/LiCl/DMAc exhibited remarkable stability at 4 °C as no significant degradation of the cellulose occurred.

Direct relationship between M_r and polymer size are usually represented in the scaling law [44–46]: $\sqrt{\langle r_g^2 \rangle} = QM_r^q$. Fig. 3 shows the log–log plot of the root mean square (rms) radius ($\sqrt{\langle r_g^2 \rangle}$) versus M_r for W-0m, W2-10m and W8-10m. The scaling factor q is the gradient of the plot. As polymer dimensions depend on polymer–solvent interactions, q yields information on the macromolecular conformation of the polymer in solution. The same linear relationship obtained indicates the cellulose in the 3 different samples adopts similar conformation in solution. The positive gradient indicates no aggregation occurs, as the latter would result in inconsistent gradients [47]. The values of the scaling factor q are very close to 0.6 (Table 3). This points to a random coil conformation of the polymer chains on the one hand, and on the other, to a good quality of the solvent. For W2-10m, the value of q slightly above 0.6 translates a somewhat stiffer conformation of cellulose than in the other two samples, and tends to confirm the hypothesis of possible slight associations of molecules forming with time upon standing for several months.

5. Conclusions

Although more labour intensive than the ‘one-pot’ method at high temperature, the water swelling and solvent

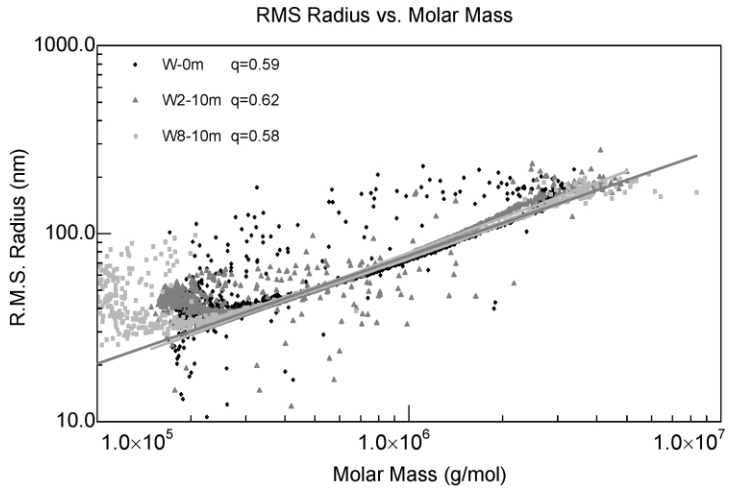

Fig. 3. Overlaid rms radii versus M_r (log–log) of W-0m, W2-10m and W8-10m.

exchange activation achieved better, faster and more reproducible subsequent dissolution, initially at ambient temperature, and completion at 4 °C. Moreover, degradation of cellulose when submitted to high temperatures was a major concern. Indeed the results obtained with the hot activation/dissolution method, namely of irreproducible efficiency and incomplete dissolution, and the yellowing associated with potential degradation at high temperature were not acceptable. Also, the possibility of Maillard reactions occurring between sugars and proteins, and leading to browning could not be ruled out when performing activation at high temperature with samples where residual gelatine could be present. The final procedure adopted was validated with a broad range of model and historic papers containing various additives used in traditional paper-making. The experiments carried out to test the stability of the solutions over time proved that the dissolution method and the storage at low temperature were very adequate leading to no significant depolymerisation nor aggregation over several months.

Acknowledgements

This research, financially supported by the Charles E. Culpeper Foundation, was carried out at the National Gallery of Art, Washington, DC, US. Warm thanks to Prof. E.R. de la Rie, National Gallery of Art for his support and guidance, and to Dr C. Shahani, Library of Congress, Washington, DC, US, for providing the technical and instrumental support. The author is grateful to Dr G. Harrison, Library of Congress, for practical help and advice.

References

[1] Huglin M. Light scattering from polymer solutions. New York: Academic Press; 1972.
[2] Kwolek SL, Morgan PW, Schaefgen JR, Gulrich LW. Macromolecules 1977;10:1390.
[3] Austin PR. Chitin solutions, US Patent No. 4,059,457; 1977.
[4] Gagnaire D, Saint-Germain J, Vincendon M. J Appl Polym Sci, Appl Polym Symp 1983;37:261.
[5] McCormick CL, Lichatowich J. Polym Sci, Polym Lett Ed 1979;17:479.
[6] McCormick CL. US Patent No. 4,278,790; 1981.
[7] Turbak AF. US Patent No. 4,302,252; 1981.
[8] Dawsey TR, McCormick CL. J Macromol Sci—Rev Macromol Chem Phys 1990;C30(384):405.
[9] Ekmanis JL, Turbak AF. Lab Highlights 251, Waters Chromatography Division, Millipore, Milford; 1986.
[10] Ekmanis JL. Am Lab News 1987;Jan–Feb:10.
[11] McCormick CL, Callais PA, Hutchinson Jr BH. Macromolecules 1985;18:2394.
[12] El-Kafrawy A. J Appl Polym Sci 1982;27:2435.
[13] Turback AF. Tappi J 1984;67(1):94.
[14] Morgenstern B, Kammer HW. Trends Polym Sci 1996;4(3):87.
[15] Brendler E, Fischer S, Leipner H. Cellulose 2001;8:283.
[16] Koch W, Herlinger H. Textil Praxis Int 1984;39(9):902.
[17] Striegel AM, Timpa JD. Strategies in size exclusion chromatography. ACS Symp Series 635, Am Chem Soc: Washington, DC 1996;366.
[18] Silva AA, Laver ML. Tappi J 1997;80(6):173.
[19] Timpa JD. J Agric Food Chem 1991;39:270.
[20] Terbojevich M, Cosani A, Conio G, Ciferri A, Bianchi E. Macromolecules 1985;18:640.
[21] Potthast A, Rosenau T, Sartori J, Sixta H, Kosma P. Polymer 2003;44:7.
[22] Striegel AM, Timpa JD. Carbohydr Res 1995;267:271.
[23] Potthast A, Rosenau T, Buchner R, Röder T, Ebner G, Bruglachner H, Sixta H, Kosma P. Cellulose 2002;9:41.
[24] Rinaudo M. J Appl Polym Sci, Polym Symp 1993;52:11.
[25] Sjöholm E, Gustafsson K, Eriksson B, Brown W, Colmsjö A. Carbohydr Polym 2000;41:153.
[26] Strlic M, Kolenc J, Kolar J, Pihlar B. J Chromatogr A 2002;964:47.
[27] Röder T, Morgenstern B, Schelosky N, Glatter O. Polymer 2001;42:6765.
[28] Röder T, Morgenstern B, Glatter O, Macromolecular symposium 162, New York: Wiley; 2000. p. 87.
[29] Sjöholm E, Gustafsson K, Pettersson B, Colmsjö A. Carbohydr Polym 1997;32:57.
[30] Kennedy JF, Rivera ZS, White CA, Lloyd LL, Warner FP. Cellulose Chem Technol 1990;24(3):319.
[31] Pionteck H, Berger W. Cellulose 1996;3:127.
[32] Matsumoto T, Tatsumi D, Tamai N, Takaki T. Cellulose 2001;8:275.
[33] Johnson DC. Cellulose chemistry and its applications. New York: Wiley; 1985. Chapter 7.
[34] Turbak AF. Wood and agricultural residues. New York: Academic Press; 1983. p. 87.
[35] Strlič M, Kolar J, Žigon M, Pihlar B. J Chromatogr A 1998;805:93.
[36] Jerosch H. Evaluation de l'état de dégradation de la cellulose/holocellulose dans différents types de papiers par chromatographie d'exclusion stérique, Thèse de Doctorat, Université Versailles-St. Quentin-En-Yvelines; 2002.
[37] Debzi El M. Celluloses issues du traitement à la vapeur: évolution des masses moléculaires moyennês, transformations morphologiques et cristallines, Thèse de Doctorat, Université Joseph Fournier—Grenoble I; 1992.
[38] T 412 om-94, TAPPI test methods, Technical Association of the Pulp and Paper Industry, Atlanta, US, TAPPI Press; 1994.
[39] Timpa JD, Ramey Jr HH. Text Res J 1989;59(11):661.
[40] Potthast A, Rosenau T, Sixta H, Kosma P. Tetrahedron Lett 2002;43:7757.
[41] Dupont A-L. Gelatine sizing of paper and its impact on the degradation of cellulose during aging; a study using size-exclusion chromatography, PhD Thesis, University of Amsterdam; 2003.
[42] Dupont A-L, Harrison G. Biomacromolecules; submitted.
[43] Dupont A-L. In: Daniels V, Donithorne A, Smith P, editors. IIC Congress: works of art on paper, books, documents and photographs, techniques and conservation. London: International Institute for Conservation; 2002. p. 59.
[44] Pincus P. Macromolecules 1976;9:386.
[45] De Gennes PG. Scaling concepts in polymer physics. Ithaca: Cornell University Press; 1979.
[46] Laguna MTR, Medrano R, Plana MP, Tarazona MP. J Chromatogr A 2001;919:1.
[47] Olieman C, Tromp RH. Oral presentation of International Symposium on Separation and Characterization of Natural and Synthetic Macromolecules, Amsterdam, The Netherlands; 5–7 February 2003.