



Physical Properties of Carboxymethyl Cellulose (I): Solubility, Conformation and Supramolecular Aggregation

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ABSTRACT

Carboxymethyl cellulose (CMC), commonly used as the sodium salt (NaCMC) and also known as cellulose gum, carmellose or E466, is an ionic cellulose ether widely used in foods, pharmaceuticals, drilling fluids, detergents, paper products and lithium-ion battery slurries. Its physical properties depend strongly on the degree and pattern of substitution, which control crystallinity, water solubility, chain conformation, supramolecular aggregation and rheology. The aim of this article is to review current understanding of these relationships. We focus on how average degree of substitution and chemical heterogeneity determine whether CMC is molecularly dissolved or forms colloidal aggregates. A compilation of experimental results indicates that, for samples with approximately fewer than one carboxymethyl group per anhydroglucose unit, most chains are molecularly dissolved while a smaller fraction forms fringed-micelle aggregates. Block-like unsubstituted sequences promote crystallinity, aggregation, thixotropy, and physical gel formation. More uniformly substituted samples exhibit smooth shear-thinning behavior. We also discuss the methods used to characterize CMC, its historical development and industrial applications, and common limitations in the literature. We conclude by providing recommendations for measuring and reporting degree of substitution, molar mass, intrinsic viscosity, solubility, and aggregate content.

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1. Introduction

Carboxymethyl cellulose, typically used as the sodium salt (NaCMC), is an anionic cellulose ether and the most widely produced ionic cellulose derivative.^[1] Commercial and regulatory names include cellulose gum, CMC gum, carmellose, and in food labeling as E466. It is a weak, highly charged, semiflexible polyelectrolyte which is featured in many formulated products, including foods, beverages, toothpastes, adhesives and drilling muds.

Industrial production of CMC uses the slurry process: purified cellulose (typically from wood pulp or cotton linters) is suspended in an organic solvent such as isopropanol followed by the addition of NaOH.^[2–6] This produces a slurry that swells but does

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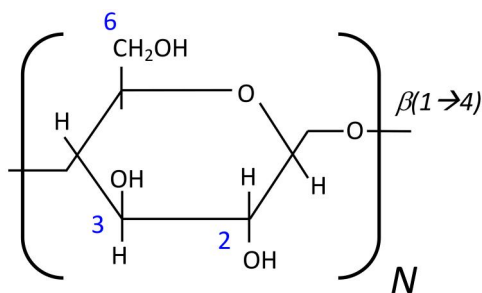


Figure 1. Repeating unit of cellulose. The carbon to which each of the three OH groups is attached is labeled by the blue numbers. Monomers are linked by β (1 $\rightarrow$ 4) glycosidic bonds.

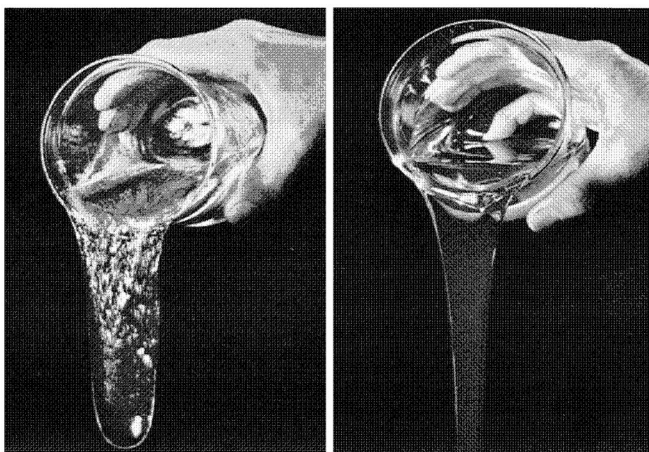


Figure 2. Illustration of flow properties of carboxymethyl cellulose with heterogeneous (left) and homogeneous (right) substitution patterns. Figure reproduced from ref^[8]

not dissolve cellulose.^[7] Chloroacetic acid or its sodium salt is added to introduce carboxymethyl groups *via* etherification. The structure of the cellulose monomer is shown in Figure 1. The H in the hydroxyl groups can be substituted by CH₂COONa. The number of carboxymethyl groups per monomer (maximum of 3) is known as the degree of substitution (DS).

Commercial NaCMC polymers typically have DS = 0.6–1.4 and molar masses of 60–1200 kg/mol. DS refers to the average over all chains in the sample, but there exists a distribution of DS values for different chains (first order heterogeneity). Further, within a single chain, different regions may exhibit different substitution patterns (second order heterogeneity). As the average DS increases, the substitution becomes more homogeneous. Samples with DS $\geq$ 1 are labeled ‘highly substituted’ and possess a relatively uniform substitution along the chain that hinders inter-chain associations. Solutions of such CMCs are shear thinning but do not gel at high concentrations and are non-thixotropic.^[9–13] These are usually marketed as possessing ‘smooth’ flow behavior.

Samples with DS $\approx$ 0.7–0.9 typically contain around 20 to 40% unsubstituted monomers, leading to the formation of unsubstituted blocks along the chain, unless specific synthesis methods are used to ensure uniformity of substitution.^[14–18] Weakly

substituted samples form physical gels at high concentrations (typically above a few weight percent) and can exhibit thixotropy, where the solution viscosity depends on the sample's shear history.

The difference in flow behavior between highly substituted and weakly substituted samples can be gauged by a simple proto-rheological experiment^[19] displayed in Figure 2. A solution of a highly substituted CMC flows as a homogeneous viscous liquid while that of a weakly substituted grade displays high elasticity and inhomogeneous flow behavior.

Commercial grades of CMC are divided into technical, semi-purified, purified, and extra-purified or food grade, see Table 1. The main impurities are sodium chloride and sodium glycolate, see Refs.^[3,20] Applications in food, drinks and pharmaceutical products typically require high purity grades while detergents and drilling fluids normally employ lower purity, cheaper grades. Some physical properties of NaCMC are listed in Table 2.

Table 1. Typical NaCMC quality grades and composition.

Grade	Example application areas	CMC content [wt %]	Salt content [wt %]
Technical	detergents, mining flotation	<75	>25
Semi purified	oil and gas drilling muds	75–85	15–25
Purified	paper coating, textile sizing and printing, ceramic glazing, oil drilling muds	>98	<2
Extra purified	food, toothpaste, pharmaceuticals	>99.5	<0.5

Adapted from Ref.^[3]

Table 2. Properties of extra-purified commercial NaCMC grades.

Property	Value
Bulk Density (powder) [g/mL]	0.5–1
Monomer molar mass	$162 + 80 \times \text{DS}$
Partial molar volume [$\text{cm}^3 \text{mol}^{-1}$]	$92.4 + 26.5 \times \text{DS}$
Partial molar adiabatic compressibility [$\text{cm}^3 \text{mol}^{-1} \text{bar}^{-1}$]	$-(22.2 + 35.9 \times \text{DS})$
Length of chemical monomer	$\approx 0.5 \text{ nm}$
Intrinsic dissociation constant	3–3.4
pH (1 wt % solution)	8
Surface tension	not surface active
Refractive index	≈ 1.51
Film tensile strength	55–103 MPa

Data from Refs.^[8,21–23]

1.1. Scope of this review

Several reviews have addressed aspects of CMC applications. The survey by Feddersen^[8] examined a broad range of industrial uses, as did other early reviews.^[24–26] Recent reviews^[5,27–33] have focused on academic research and potential applications of CMC and its derivatives but have not examined actual industrial practices. A survey of this type would help academic researchers understand current industrial challenges. The most extensive modern review covering physical properties of CMC is found in Ref.^[34]

Here we provide an overview of how chemical composition governs solubility, aggregation, and supramolecular structure. The relationship of these with the flow properties of concentrated solutions and gels will be discussed in a subsequent manuscript. Ways to improve research on CMC solutions and gels are outlined in the conclusions.

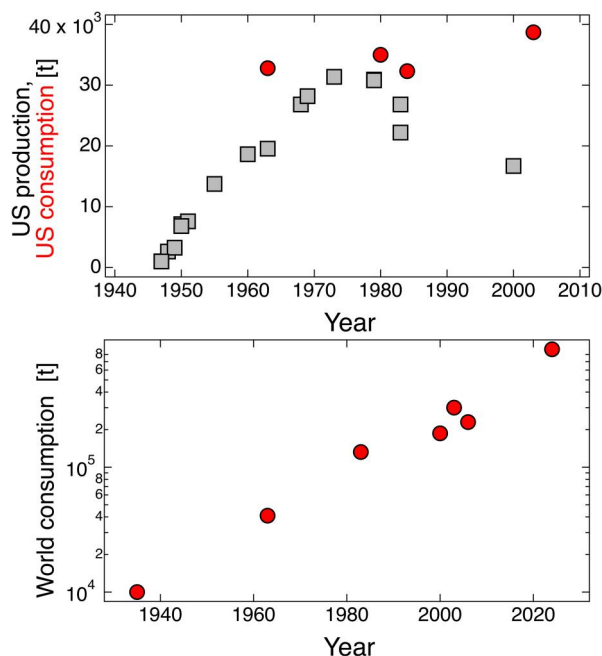


Figure 3. CMC consumption and production in the US (top) and worldwide (bottom). Data from Refs.^[25,26,35–40]

Applications are summarized, from the historical development of CMC to current industrial uses (Figure 3).

Section 2 reviews the historical development and economic importance of NaCMC. Current applications and how specific properties of CMC enable these are summarized in Section 3. Sections 4 and 5 provide an extensive review of the chemical composition and macroscopic solubility of CMC. The conformation of individual polymer chains as well as their aggregates is discussed in Sections 6 and 7. Scattering, viscosity and microscopy data show that CMC solutions display both *molecular* and *colloidal* solubility. In the concluding sections, we provide a brief summary of the rheological properties of CMC and how these arise from the various physical phenomena discussed throughout the review, identify common problems in the literature and give some recommendations to improve the quality of research on CMC.

2. History, production and economic importance of carboxymethyl cellulose

Sodium carboxymethyl cellulose (NaCMC), first synthesized over 100 years ago in Germany by Jansen^[41] as a gelatin substitute, gained industrial relevance in the 1930s in detergent formulations under the name Tylose HBR, a low purity ($\approx 30\%$) grade, when it was found that addition of CMC to detergents reduced the amount of surfactant required for washing. During and after WWII it was used in detergent formulations in Germany,^[25] with an average annual production of 10⁷ kg,^[42,43] and in other European countries,^[44,45] owing to the shortage of fatty acids.^[44] A review of the academic literature and US patents up to 1945 shows a large number of proposed uses in

the textile and paper industries.^[24] Many other uses, for example as a dye stabilizer or in paints due to its good film forming properties, were also proposed. Despite these many uses, the US production remained modest at $\simeq 1 \times 10^6$ kg/year. A report by Hoyt in 1945 on the Kalle chemical plant of IG Farbenindustrie,^[42] and subsequent research by Vaughn and Smith^[46] from Wyandotte Chemicals Corporation, led to increased NaCMC use in U.S. laundry detergents^[45,47] and a sharp rise in production. By 1951, yearly production in the U.S. had reached 8×10^6 kg, roughly two thirds of which were used in detergents,^[25] with additional uses in drilling fluids and textiles.

The introduction of purified NaCMC^[22,25] by Hercules in 1946 led to its use as a thickener and structuring agent in food products,^[26,48] an application that persists to the present day. By the 1980s, the global consumption of NaCMC exceeded 10^8 kg/year. Today NaCMC is primarily used in food and beverage products, where it acts as a thickener, emulsifier and humectant as well as in oil drilling fluids. Other applications include its use as a structuring component in dentifrices^[49,50] and as an adhesive in the paper industry, see [Section 3](#).

[Figure 3](#) plots the consumption of CMC in the United States and worldwide as a function of year. According to market reports,^[40,51] global production in 2025 was approximately 8.8×10^5 tonnes per annum, which corresponds to a market value of $\simeq 2$ billion USD. The total value of cross border trade was $\simeq 1.2$ billion USD, with China, the Netherlands and Finland being the main three exporters.^[52]

3. Industrial applications and formulation of carboxymethyl cellulose

The rheological, solubility, osmotic and adhesive properties of CMC, as well as its complexing ability with oppositely charged soft matter, underpin its role in many industrial applications. Its biodegradability and cellulose-derived structure also make it relevant to sustainability-driven replacement of petroleum-based synthetic polymers. For example, the high osmotic pressure of CMC solutions in water decreases the water activity and allows it to function as a moisture retainer in baked products. The pH dependence of CMC solubility is exploited in pharmaceutical formulations, where it is used as a coating agent, which does not dissolve in the acidic gastric juice but is dissolved in the small intestine. On the other hand, the insolubility in acidic media limits its application in wallpaper coatings due to precipitation when it comes in contact with sizing agents.^[53]

Below we review some of the main aspects of NaCMC processing and then summarize the applications in specific fields, focusing on how the properties of CMC and its interaction with the other formulation components influence the product performance.

3.1. Processing and formulation

NaCMC is usually supplied as a powder, whereas industrial applications generally require dissolution in aqueous media at concentrations ranging from a few weight percent (oil-drilling fluids, toothpastes) to under 100 ppm (wines). Typical environments include tap water, which is usually neutral or slightly alkaline and contains calcium and magnesium carbonate concentrations of $\simeq 0$ – 0.5 mM in soft water and $\simeq 1$ – 2 mM in hard water.^[54] These concentrations are much lower than those of seawater, relevant to

older drilling processes, which contains $\simeq 0.5$ M Na^+ and Cl^- ions and $\simeq 50$ mM Mg^{2+} . Formulated products span a broad pH range. Milk products are slightly acidic (pH $\simeq 6.5$ – 6.8), while citrus juices typically have pH values of 2–4. In pharmaceutical applications, the relevant environment can also include gastric juice, which has pH $\simeq 2$, where CMC is insoluble, see Section 5.2.

In industrial processing, for example during toothpaste manufacture, CMC powder is introduced into a mixing vessel under strong agitation to promote dissolution. Commercial NaCMC powders typically contain $\simeq 10$ wt% moisture, corresponding to the equilibrium moisture uptake at $\simeq 20\%$ relative humidity according to Feddersen.^[8] The absorbed water content increases to around 30 wt% at 80% relative humidity and depends only modestly on DS in the range 0.7–1.2.^[8] Somewhat different equilibrium moisture contents were reported by Klug^[55] and Berlin et al.^[56]

Commercial grades are available with different particle sizes, with smaller particles dissolving more rapidly. Direct addition of large amounts of NaCMC powder to water leads to lump formation: a swollen gel layer forms around partially hydrated particles. The interior remains dry until the outer gel layer slowly dissolves.^[57–59] To minimize this problem, the powder can first be dispersed in a non-solvent such as glycerol or ethylene carbonate,^[60,61] followed by gradual addition of water so that individual granules hydrate separately. This procedure produces much faster dissolution. Dispersion in low molar mass solids such as sucrose also helps suppress lump formation. Higher degrees of substitution typically dissolve faster than lower ones because gel formation is suppressed. Finally, we note that air trapped within the powder particles introduces bubbles during dissolution, which may need to be removed after dissolution is complete.

If salts are present in the final formulation, they are generally added after dissolution of the CMC. Addition of salt before dissolution slows dissolution of the polymer, presumably because the free-energy gain upon dissolution of the polyelectrolyte is reduced.^[62] Some studies^[63,64] and commercial brochures^[22] report lower viscosities when salts are added before the polymer. This likely reflects incomplete dissolution caused by slow dissolution kinetics in salt solutions. If sufficient time is allowed for complete dissolution, the final viscosity is independent of whether the salt or polymer is added first.^[12,13]

Commercial brochures often state that the viscosity of NaCMC solutions continues to increase for hours or even days after dissolution. These slow kinetics are generally attributed to gradual aggregate and/or network formation, although systematic studies demonstrating this behavior are lacking. Related observations have been reported for the influence of mixing conditions. Elliot and Ganz reported that high-shear mixing promotes formation of strong gels that can subsequently be disrupted by slow shear, see Ref.^[65] and references therein. These observations are qualitative in nature and have not been verified in recent work using modern rheometers.

Processing at elevated temperatures generally causes hydrolytic degradation of the CMC chains, with a corresponding decrease in solution viscosity due to a decrease in N . Depolymerization may also occur if the CMC chains are subjected to strong shear flows.^[66] A slow decrease in viscosity at room temperature has also been reported, which likely also occurs due to slow hydrolysis of the CMC backbone.^[67] In industrial

formulations, preservatives such as sodium or potassium sorbate and sodium benzoate are commonly used to suppress microbiological degradation.

3.2. CMC in food products

CMC is an important polymer in the food and beverage industries, where high-purity NaCMC is employed as a thickener, stabilizer, and emulsion modifier in baked goods, sauces, beverages, and dairy formulations.^[68–75] CMC also acts to prevent ice crystal formation. Market analyses^[51,76] indicate that the food and beverage segment accounts for the largest share of global CMC consumption ($\simeq 40\%$), reflecting its regulatory approval in major markets such as the United States, the European Union^[77] and China. The use of NaCMC in processed foods dates back to the 1950s as can be seen in the extensive patent literature, including stabilizer systems for ice creams and frozen desserts,^[78–81] dairy products,^[82–84] wine and tartarate clarification,^[85,86] and baked goods.^[87–89]

3.3. CMC for wine stabilization

CMC is used in white wines at low concentrations (≤ 0.1 g/L)^[90] as a crystallization inhibitor to prevent potassium hydrogen tartrate crystal formation.^[91–95] NaCMC has been reported to have little or no sensory impact in dry white wines.^[96] Sommer^[75] evaluated CMC for protein removal, because it is known to precipitate proteins.^[97,98] The protein-removal efficiency depends on the specific wine and does not outperform the more common method of protein removal with bentonite.^[75] In red wines, haze formation limits the usefulness of CMC,^[99,100] though some studies suggest that it may be useful for specific types of red wines.^[101]

3.4. CMC in oil-drilling fluids

CMC is also used widely in oil drilling fluids,^[51,102] where it is mixed at concentrations of a few weight percent with salty water and clays to generate viscous gels. Market reports usually assign $\simeq 20\%$ of global CMC production to oil drilling applications. Its main functions are to act as a thickener (i.e. viscosifier) that prevents fluid loss into porous rocks and stabilizer that reduces shale hydration and prevents borehole collapse.^[103–105] A recent overview of NaCMC in oil-drilling fluids can be found in Ref.^[106]

3.5. CMC in laundry detergents

The first major industrial use of CMC dates to the Second World War, when it was found that addition of CMC improved the performance of laundry detergents. While displaying no active detergency, NaCMC adsorbs to cellulose fibers preventing soil re-deposition to cotton textiles during the laundry process. This is known as the ‘protective colloid’ function.^[107–110] The amount of NaCMC added to liquid and powder detergents depends on the water hardness and varies widely across different formulations, with higher contents of up to 10 wt%^[111,112] (Table 3).

Table 3. Industrial applications of carboxymethyl cellulose, along with key functions and relevant physical properties.

Industry	Grade	Relevant Properties	Example products	Function	Refs
Adhesives	Industrial	Film-forming, cold-water solubility, specific-surface adhesion, non-staining films	Wallpaper, denture adhesives	Adhesive	[113,114]
Agriculture	Industrial	Viscosity, biocompatibility, thixotropy, adhesion, osmotic pressure [†]	Pesticide emulsions, slow-release fertilizers, seed coatings	Protective colloid, suspension stabilizer, viscosifier, water retention	[115–117]
Ceramics and Construction materials	Technical	Viscosity, burnability, adsorption to particles	ceramic tiles, sanitary ware ^a	Suspending agent, binder, plasticizer	[118–121]
Coatings & Paints	Industrial	Viscosity, shear thinning	Emulsion paints	viscosifying agent, binder, suspending agent	[122,123]
Cosmetics	Cosmetic	viscosity, shear thinning, moisture retention	Toothpastes, hand creams, shampoos, hair gels	Thickener, suspending agent, humectant, improve emulsion stability, lubricant	[124–126]
Detergents* ^b	Industrial	Adsorption to cellulose surfaces, dissolution rate, stability in the presence of surfactants, divalent ion binding	Laundry detergents, surface cleaners, dishwashing liquids	Dispersing agent, anti-soil redeposition, water-softening	[127–131]
Drinks	Food	Viscosity, gel strength, acidic solubility	soft drinks, concentrates, milk beverages	Stabilizer, mouthfeel, viscosifier, suspending agent, texture	[132–138]
Oil and Gas* ^c	Industrial	Viscosity, shear thinning, gel strength, solubility in salt solutions ^d	Drilling fluids	Suspends solids, provides yield stress [‡] , prevents fluid loss into rock formations	[106,139–142]
Firefighting	Industrial	Viscosity, adhesion	Fire-suppressant gel	Thickener, adhesion to surfaces	[143]
Foods* ^e	Food-grade	Viscosity, gel strength, osmotic pressure, acidic solubility	Cake mixes, ground meats, pet foods, fruit jams, sauces, dressings, ice-creams, puddings, spreads, doughs	Thickening, water binding, prevents ice crystallization, mouthfeel, lubricant, film former	[144–147]
Paper	Industrial	Film-forming, binding, osmotic pressure, tensile strength	paper, tissues, packaging materials	Improve adhesion and strength, grease resistance, printability	[148–151]
Pharmaceuticals* ^f	Pharmaceutical	pH-responsive solubility, biocompatibility, dissolution kinetics	tablets, ophthalmic solutions, nasal and topical sprays, wound dressing	Excipient, suspending agent, thickening agent, controlled release, moisture retainer (humectant), absorber, anti-adhesion barrier	[28,33,152–160]
Textiles	Industrial	Film-forming, reaction with dyes	Woven cotton fabrics ^a	Sizing agent (protective coating), viscosifier for printing pastes	[161–163]
Wines	Food-grade	colloidal stability, low sensory impact at low concentration	White wines	Prevents tartaric acid crystallization	[164,165]

* indicates major industrial uses. [†]Osmotic pressure of solutions and gels dictates water-retention capacity and swelling. Information gathered from ^[8,166,167] and references cited in the last column. ^a CMC is used in the manufacture but is not present in the final product ^b Primarily laundry detergents, but also dishwashing liquids and hard-surface cleaners. ^c yield stress typically develops when mixed with clays or other colloids ^d for example for drilling muds prepared with seawater.

3.6. CMC in personal-care products

In personal care and cosmetic products, CMC functions as a rheology modifier in shampoos, lotions and dentifrices, where its water-retaining (humectant) behavior and film-forming properties are exploited.^[168,169]

3.7. CMC in batteries, cement, paper and additive manufacturing

In cement systems, NaCMC serves as a water retention agent that enhances workability and adhesion.^[168] In lithium-ion batteries, CMC is used as a dispersant and binder for electrode slurries,^[170–173] where sustainability considerations have motivated interest in water-processable and bio-derived binders.^[174–179] An overview of how CMC influences the rheological properties and performance of battery slurries can be found in Ref.^[180] Recently, the use of NaCMC as a component for 3D-printed hydrogels and aerogels has been explored.^[181–184] In paper manufacture, it improves fiber bonding and surface strength.^[185,186] Potential uses of NaCMC in food, textiles, biomedical engineering, pharmaceutical formulations, wastewater treatment and energy storage are covered in an extensive review published recently by Rahman *et al.*^[5]

4. Degree of substitution and chemical heterogeneity

CMC samples display several levels of chemical heterogeneity. The average degree of substitution gives the mean number of carboxymethyl groups per glucose unit, but does not specify which hydroxyl positions are substituted, how substituents are distributed along a chain, or how the substitution varies between chains see Figure 5. These distinctions are important because they influence solubility, crystallinity, supramolecular aggregation and flow behavior. In this section, we summarize the main methods and results used to describe substitution patterns, compositional heterogeneity and crystallinity in CMC polymers. Molar mass dispersity is also discussed.

4.1. Substitution patterns

The Spurlin model^[187] describes the kinetics of substitution of cellulose ethers, assuming that the ratio of the reaction constants (k_i) for the three positions does not change with time. The fraction of monomers with position i substituted is:

$$x_i = 1 - e^{-k_i t} \quad (1)$$

where t is the reaction time and $i = 2, 3, 6$ corresponds to each of the positions in Figure 1.

The fraction of monomers which are unsubstituted (χ_0), mono-substituted (χ_1), di-substituted (χ_2), or tri-substituted (χ_3) are:

$$\chi_0 = e^{-(k_2+k_3+k_6)t} \quad (2)$$

$$\chi_1 = e^{-(k_2+k_3)t} + e^{-(k_2+k_6)t} + e^{-(k_3+k_6)t} - 3e^{-(k_2+k_3+k_6)t} \quad (3)$$

$$\chi_2 = e^{-k_2 t} + e^{-k_3 t} + e^{-k_6 t} - 2e^{-(k_2+k_3)t} - 2e^{-(k_2+k_6)t} - 2e^{-(k_3+k_6)t} + 3e^{-(k_2+k_3+k_6)t} \quad (4)$$

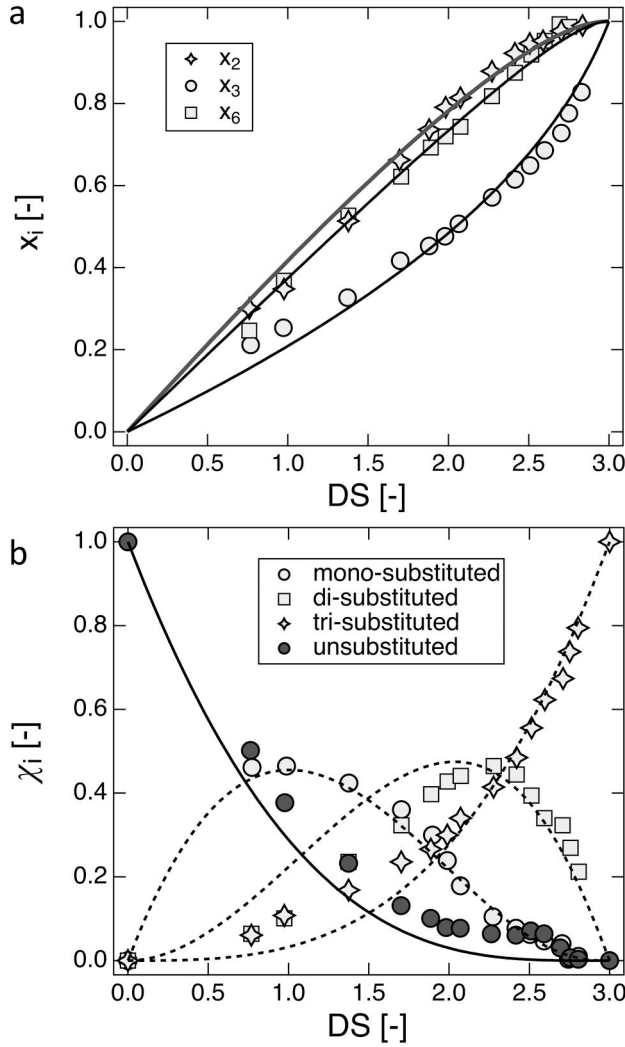


Figure 4. a: partial degrees of substitution for each position as a function of total degree of substitution for CMC samples synthesized by carboxymethylation of cellulose with chloroacetic acid in IPA/NaOH. Data are from Ref.^[188] Lines are the Spurlin model (Eq. 1). The best fit reaction constants are $k_2 : k_3 : k_6 = 2.3:1:2$. b: Fraction of monomers with varying types of substitution patterns as a function of degree of substitution for the same samples as part a. Lines are the Spurlin model (Eqs. 2–5) with the reaction constants obtained in the fit of part a.

$$\chi_3 = 1 - e^{-k_2 t} - e^{-k_3 t} - e^{-k_6 t} + e^{-(k_2+k_3)t} + e^{-(k_2+k_6)t} + e^{-(k_3+k_6)t} - e^{-(k_2+k_3+k_6)t} \quad (5)$$

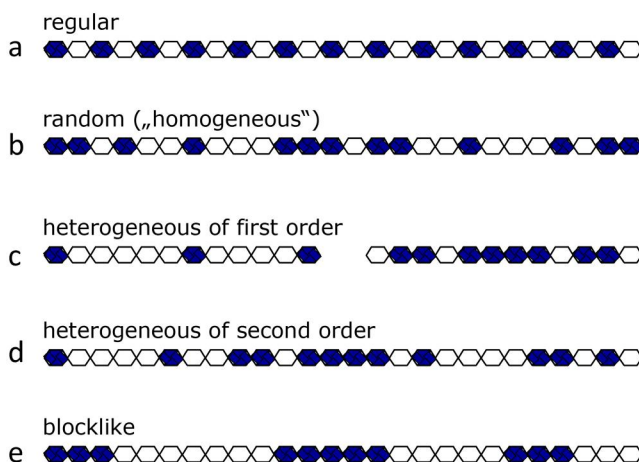
Note that we omit the last term of Equation 17 of Ref.^[187], which appears to be a typo.

Figure 4 considers the application of the Spurlin model to experimental data for NaCMC of different degrees of substitution. Kono *et al.*^[188,189] synthesized a series of NaCMC samples by carboxymethylating fibrous cellulose with chloroacetic acid in concentrated NaOH water/isopropanol media. ¹³C NMR was used to determine the

Table 4. Reaction constants of Spurlin model according to various literature sources.

Reference	k_2	k_3	k_6
Baar <i>et al.</i> ^[190]	3	1	2.1
Kragten <i>et al.</i> ^[191]	1.8	1	1.2
Kragten <i>et al.</i> ^[191]	1.9	1	1.3
Kragten <i>et al.</i> ^[191]	2.3	1	1.5
Zeller <i>et al.</i> ^[192] ^a	2.35	1	1.82
Abdel-Malik & Yalpani ^[193] ^b	2.1	1	1.5
Niemela & Sjostrom ^[194] ^c	3.1	1	2.6
Reuben & Conner ^[195] ^a	2.14	1	1.58
Ho & Klosiewicz ^[196] ^a	2	1	1.5
Buytenhuys & Bonn ^[197] ^b	2.5	1	1.8
Croon & Purves ^[198] ^b	4.6	1	3.6
Timell & Spurlin ^[199] ^b	2	1	2.5
Kulicke <i>et al.</i> ^[200] ^a	2.6	1	2.8
Adden ^[201] *	2.6	1	1.9
Kono <i>et al.</i> ^[188] *	2.3	1	2

This table follows the compilation by Baar *et al.*^[190] and Adden^[201]. ^a obtained from a fit imposing a fixed ratio of reaction constants to a series of samples. ^b values quoted from Ref.^[190] * Calculated from data in Ref.^[188], see Figure 4 for fits of the Spurlin model to these data. ^c average of values obtained for two samples: 3.3:1:2.9 and 2.8:1:2.2.

**Figure 5.** Substitution patterns for CMC polymers. Blue hexagons represent substituted glucose units and hollow hexagons are unsubstituted ones. Figure adapted from Ref.^[202]

fractions of monomers with a given substitution pattern. The Spurlin model is shown as full and dashed lines in Figure 4. The ratios of reaction constants are determined by fitting the x_i data in part a. These values are then used to calculate χ_i as a function of degree of substitution in part b (Table 4).

The values of x_i in Figure 4a are well described by the Spurlin model. Similar agreement is observed for other systems with different ratios for the reaction constants, see for example^[200]. The data in Figure 4b show that the Spurlin model is less successful at predicting the values of χ_i , compared to x_i . In particular, the number of unsubstituted monomers is underestimated throughout the entire DS range. Reuben and Conner's data^[195] for χ_i of CMCs over a similar DS range show better agreement with the Spurlin model. Reuben^[203] modified Spurlin's model to include a k_3 constant which increases threefold for monomers where the position 2 hydroxyl has been substituted, see^[201] and references therein for additional discussion of this topic.

The Spurlin model has been extensively applied to describe substitution patterns of carboxymethyl cellulose in the literature, and is used as a reference for homogeneous substitution. Table 4 collects the reaction constants reported in various studies. These consistently show $k_2 \geq k_6 > k_3$ but the specific ratios between the three constants vary by a factor of $\simeq \times 2\text{--}3$ across different studies, presumably due to differences in the reaction conditions (solvent media, ratio of chloroacetic acid to AGU, etc.) which are known to influence the reaction kinetics.^[190,191,204] Dapia *et al.*'s data suggest that temperature influences the overall reaction constant but not the ratio between k_i s.^[205]

4.2. Compositional heterogeneity

As early as 1950,^[206] Durig and Banderet reported that strong centrifugation separates weakly substituted NaCMC into 'solution' and 'gel' fractions. Both fractions were found to have similar molar mass and average DS. The gel fraction displayed crystalline peaks in the x-ray diffraction (XRD) pattern similar to those of mercerized cellulose, presumably arising from block-like unsubstituted groups along the chain. Cellulose being insoluble in water, these unsubstituted blocks cluster together and form crystalline cores. The experiments of Elliot and coworkers^[9–11] give support to this picture and show that the solution fraction displays pseudoplastic (shear-thinning) behavior while the gel fraction exhibits thixotropy, as shown in Figure 6. The presence of a gel fraction in NaCMC samples in water is confirmed by several studies.^[10,11,207,208]

The gel fraction in CMC solutions can be measured by filtration or by elution with size exclusion chromatography. These measurements show that, for CMC samples produced by the slurry process, the gel fraction decreases with increasing degree of substitution, as shown in Figure 7. For $DS \geq 1$, the gel fraction becomes very small. This explains the absence of gelling and thixotropic behavior in highly substituted polymers and is consistent with XRD data showing no measurable crystallinity for samples with $DS \geq 0.9\text{--}1.1$,^[209,210] as discussed in Section 4.5. The specific DS at which the cross-over between weakly and highly substituted samples occurs depends on the reaction conditions used to prepare the NaCMC. For the slurry process, the cross-over between 'gelling' and 'smooth' behavior occurs at around $DS \simeq 1$.

4.3. Distribution of degree of substitution between chains

The most commonly employed methods to determine the *average* degree of substitution of CMC are titration of the acid form and ^1H NMR.^[188,211–213] Other methods, for example based on thermogravimetric analysis,^[15] complexation with an oppositely charged polyelectrolyte^[214] or scanning electron microscopy^[215] have also been developed. NMR methods also allow the determination of the partial degrees of substitution for different positions in the monomer, see Refs.^[188,189]

The heterogeneity in the degree of substitution across different CMC chains has been quantified by chromatography and capillary zone electrophoresis. Shakun *et al.*^[216] used HPLC to measure the distribution of DS in CMC samples produced by the slurry process. Two starting materials were chosen for the cellulose: microcrystalline cellulose (Avicel) and cotton linters. The standard deviation of the DS distribution of each sample is plotted as a function of average degree of substitution in Figure 8. The samples

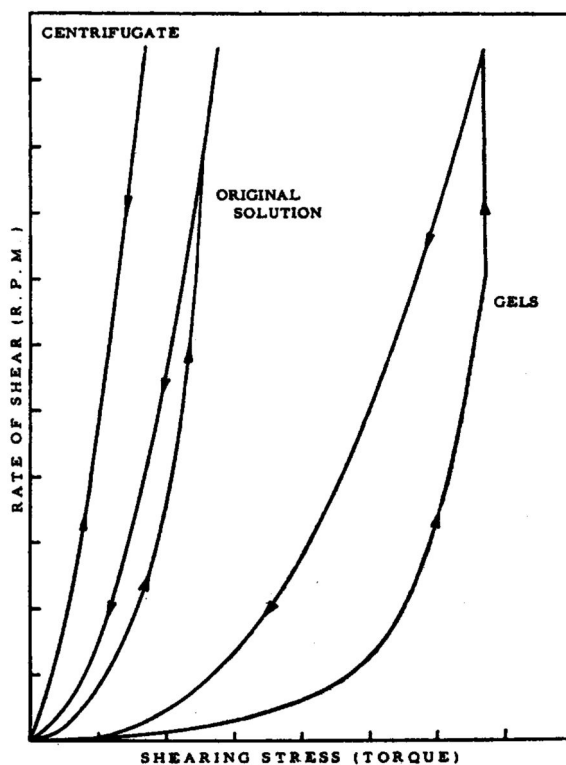


Figure 6. Rheological properties of NaCMC solution before centrifugation (original solution) and the solution and gel fractions after separation. Figure reproduced from Ref.^[10]

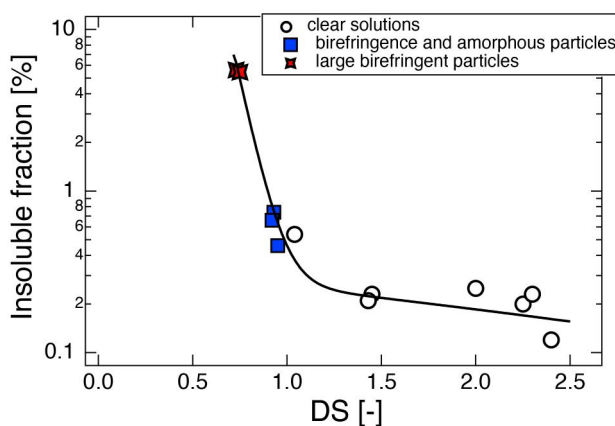


Figure 7. Mass percentage of insoluble content in NaCMC samples as a function of degree of substitution. Samples are classified according to their appearance under the microscope. Line is a guide to the eye. Data are from Ref.^[208]

generated from microcrystalline cellulose display a constant standard deviation which is independent of DS. By contrast, samples derived from cotton linters show a decreasing trend in standard deviation with increasing average DS, see Figure 8. Oudhoff *et al.*^[217] determined the distribution of DS for commercial NaCMC samples and report that a

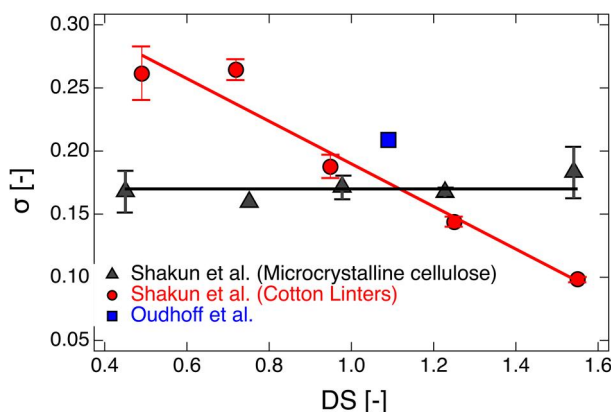


Figure 8. Standard deviation (σ) in degree of substitution of CMCs as a function of average degree of substitution. The starting cellulose materials for Shakun *et al.*'s samples are cotton linters or microcrystalline cellulose. The starting material for Oudhoff *et al.*'s samples was not reported. Lines are guides to the eye. Data are from Refs.^[216,217]

sample with average $DS = 1.09$ displayed a DS polydispersity of $\mathcal{D} = 1.04$, which corresponds to a standard deviation of ≈ 0.21 , in agreement with the results of Shakun *et al.*, see Figure 8.^[218] The starting cellulose material for their sample was not reported but is likely cotton linters or wood pulp.^[219]

Shakun *et al.*'s^[216,220] chromatography results indicate that for samples produced by a single etherification step, no correlation exists between molar mass and DS of chains within a given sample. In contrast, twice-etherified samples with high substitution (≈ 1.5) displayed a measurable correlation between these variables. These highly substituted samples contain essentially no chains with $DS < 1$, meaning that all chains are hydrophilic and their solution behavior is largely insensitive to small variations in DS. As a result, the observed correlation between DS and molar mass in these samples is unlikely to influence their flow properties.

4.4. Random vs. block-like substitution

Methods to quantify blockiness typically rely on depolymerizing the CMC chain and analyzing the resulting fragments.^[18,221–223] An example is shown in Figure 9. The enzyme endoglucanase (Econase CE, AB Enzyme) cleaves bonds between two unsubstituted glucose units but does not cleave bonds adjacent to substituted units. Stigsson *et al.*^[221] define a blockiness parameter as the ratio of glucose released by enzymatic hydrolysis to that released after acid depolymerization. This method provides a simple, although qualitative, means to characterize blockiness in substitution patterns.

As discussed in Section 8, blockiness is an important parameter for understanding the flow properties of concentrated CMC solutions and gels. Methods to quantify blockiness are therefore needed to interpret the behavior of CMC polymers in industrial formulations.

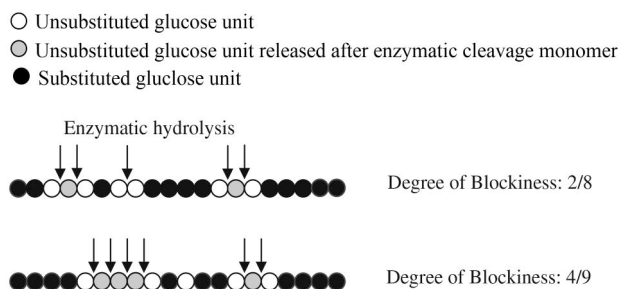


Figure 9. Example of determination of blockiness parameter using enzymatic hydrolysis. Figure adapted from Ref.^[221]

4.5. Crystallinity

Kamide *et al.*^[210] studied the structural and solubility properties of carboxymethyl cellulose as a function of degree of substitution. Two cellulose polymers with different crystal structures (Cell-I and Cell-II) were used as the starting polymers: the Cell-I crystal structure, where the polymer chains are aligned parallel to each other, corresponds to the type of cellulose found in nature, which is used to synthesize commercial samples. The Cell-II crystal structure, where chains are aligned in an anti-parallel structure, is obtained from regenerated (i.e., dissolved and precipitated) cellulose. Carboxymethylation was carried out by the slurry process, using isopropanol as the non-solvent. The CMC samples derived from Cell-I were found to display $x_2 + x_3 \simeq (1 - 1.5)x_6$. By contrast, for the CMCs synthesized from the Cell-II, some 90% of the substitution occurred at the 6 position.

X-ray diffraction (XRD) patterns for the two cellulose samples studied by Kamide *et al.* before and after alkaline addition are shown as the top two curves in Figure 10. In both cases, addition of alkali partially breaks the crystalline structure, as seen by the decrease in the prominence of the crystalline peak at $2\theta \simeq 20\text{--}22^\circ$. Carboxymethylation further decreases the presence of crystal regions and produces an amorphous halo.

A separate study by Xiquan *et al.*^[209] reported somewhat different behavior. The XRD pattern for their starting cellulose material, shown in Figure 11a, closely resembles that of Kamide *et al.* However, as the carboxymethylation proceeds, the peak moves from $2\theta \simeq 21.8^\circ$ to lower angles and eventually morphs into an amorphous halo centered at $2\theta \simeq 20.0^\circ$ for the DS = 1.06 sample. Other literature studies either show no change in the crystalline peak position, close to Kamide *et al.*'s observations or a decrease in the peak position, as reported by Xiquan *et al.*^[20,224–228] The origin of these discrepancies is not clear at present.

A more detailed analysis of Kamide *et al.*'s data is presented in Figure 12, which plots the crystalline content of NaCMC synthesized from cellulose I and cellulose II as a function of total degree of substitution. Crystalline fractions (X_C) were obtained from the XRD data in Figure 10. The sample synthesized from cellulose II displays a steady decay in X_C as a function of DS, and samples retain relatively high values of $X_C \simeq 30\%$ at DS $\simeq 0.6$. By contrast, the NaCMC synthesized from cellulose I displays a step-like decrease with DS. The lower values of X_C at the highest DS studied

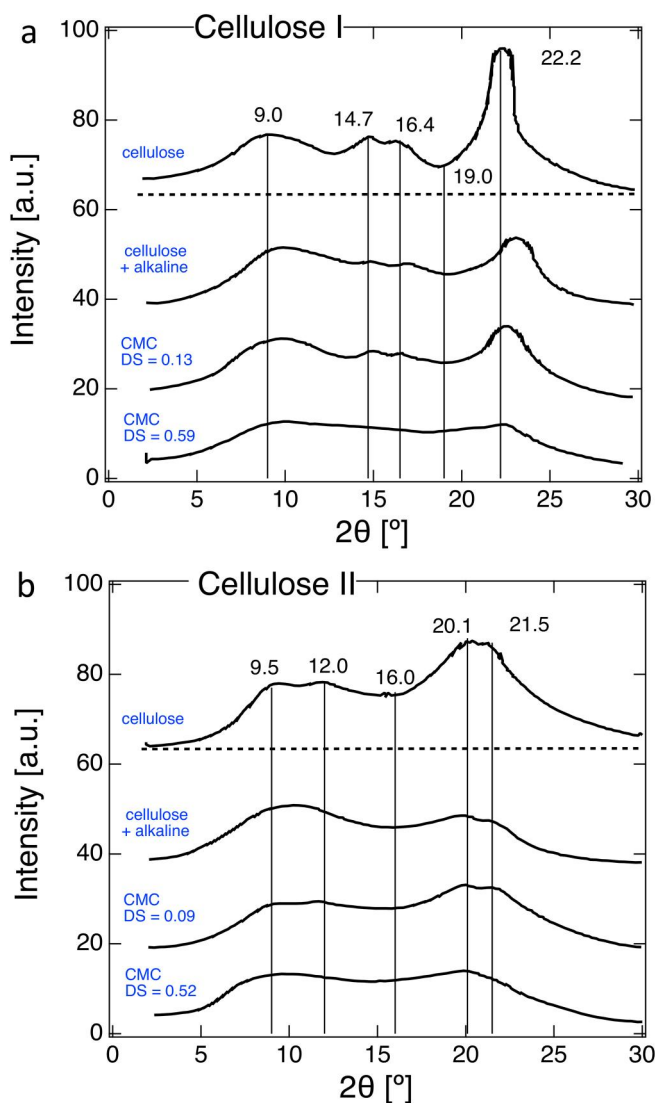


Figure 10. X-ray diffraction patterns for cellulose with different starting crystal structure (top two curves) and resulting CMCs with DS indicated on the graph. Lines indicate position of the peaks. Dashed lines are baselines for integration. Figure adapted from Ref.^[210]

are consistent with other reports, which do not observe measurable crystallinity for samples with $DS \approx 0.7$.

According to Kamide, the carboxymethylation of cellulose first occurs within the amorphous fraction and then proceeds to the crystalline parts.^[210,229] The crystalline structure of the cellulose therefore influences the reaction kinetics, as well as the substitution pattern of the CMC product. This is particularly significant for weakly substituted CMC ($DS \leq 0.7$) and presumably accounts for the differences in substitution patterns and swelling behavior observed for Kamide *et al.*'s samples.

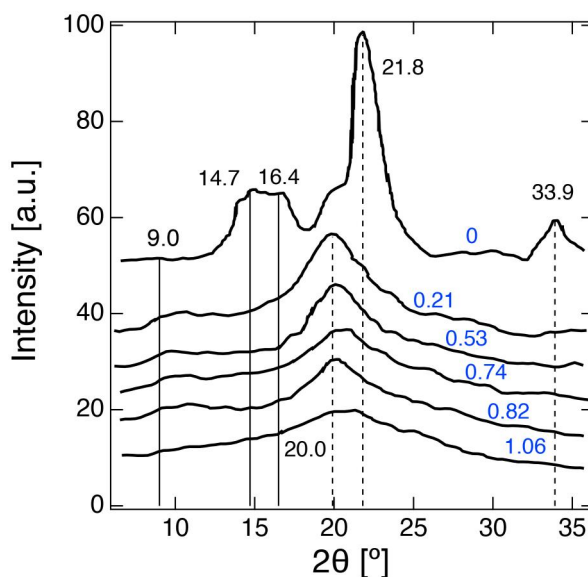


Figure 11. XRD patterns for cellulose and CMC with varying degrees of substitution, noted in blue above the curves. Full lines are θ values in Figure 10 and dashed lines indicate peak positions. Figure adapted from Ref.^[209]

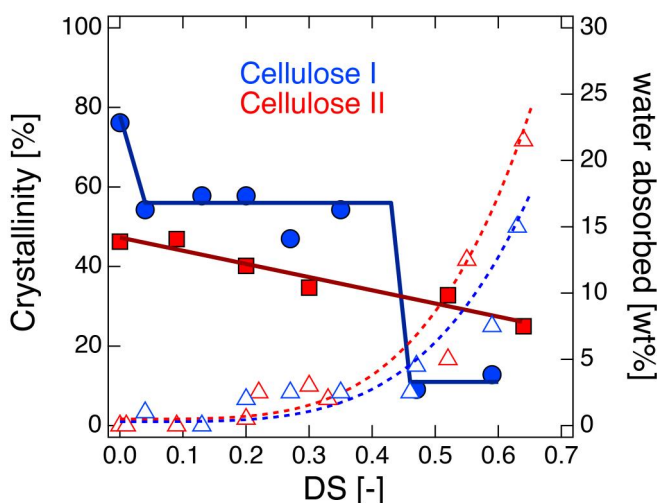


Figure 12. Percentage of crystallinity of carboxymethyl cellulose as a function of degree of substitution for two samples, where the unsubstituted cellulose ($DS = 0$) has crystal form I (full blue circles) or crystal form II (full red squares). Hollow triangles are the equilibrium water absorbed relative to the polymer's dry weight. Lines are guides to the eye. Figure adapted from Ref.^[210]

4.6. Molar mass and dispersity of commercial CMC

GPC measurements on commercial NaCMC samples show that these have molar mass polydispersities in the range of $\bar{D} = M_w/M_n \simeq 2 - 3$ ^[67,230,231]. Light scattering and membrane osmometry by Brown *et al.* give similar values of $\bar{D} \simeq 2 - 4$. An analytical ultracentrifugation study by Arinaitwe and Pawlik^[232] reported more disperse

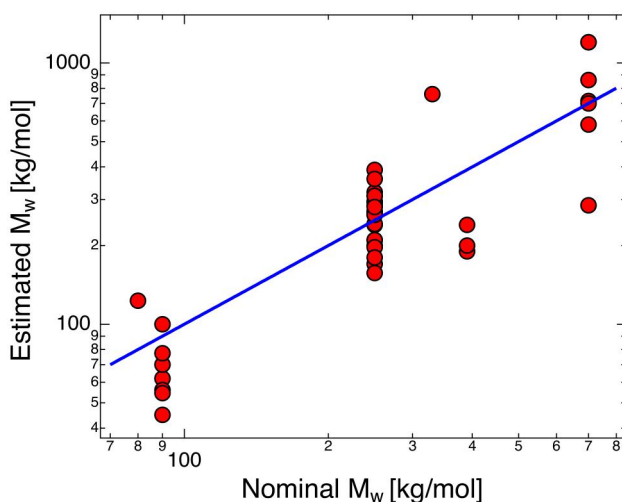


Figure 13. Estimated molar mass of commercial CMC samples as a function of their nominal molecular weight, as reported by the manufacturer. Data are from Ref.^[232] compiled in Ref.^[234] and Refs.^[12,231,235–240] The estimated molar masses are obtained from the references where reported or from $\eta_{sp} - N$ relations in Ref.^[234] otherwise. Blue line is 1:1 correspondence.

distributions $M_z/M_w \simeq 2 - 4.5$. These values are incompatible with the Schulz-Zimm (Gamma) distribution, which has been used in earlier literature^[233] to extrapolate M_z from M_w and M_n data, as this distribution allows for a maximum value of M_z/M_w of 2.

4.6.1. Accuracy of manufacturer-reported molar masses for commercial CMC

Many literature studies rely on molar mass values reported by manufacturers but these are often not accurate. Figure 13 plots the reported molar mass of some 40 commercial NaCMC samples. Large deviations between reported and measured values are observed. For the nominal 250 kg mol⁻¹ NaCMC samples, the average measured molar mass was 260 ± 61 kg mol⁻¹, which is close to the manufacturer's molar mass. However, the sample-to-sample variation was large with only 13 of 22 samples having measured molar masses within $\pm 20\%$ of the nominal value. The approximate 95% prediction interval for an individual sample was 131–390 kg mol⁻¹. Thus, the nominal molar mass is a reasonable descriptor of the average value, but it does not provide a reliable estimate of the molar mass of individual samples.

For studies reporting conformational, rheological or other dynamic properties, where the response depends on molar mass, manufacturer values for M_w should not be regarded as accurate. In this regard, using grades specified by targeted solution viscosities rather than nominal molar masses may provide a more reliable basis for reproducibility.^[178]

5. Solubility in aqueous and organic media

Hydrogen bonding and hydrophobic interactions are recognized to contribute to the insolubility of cellulose in water.^[243–246] Solubilization in water can be promoted by increasing the pH^[247–249] or by substituting the cellulose with functional groups. For

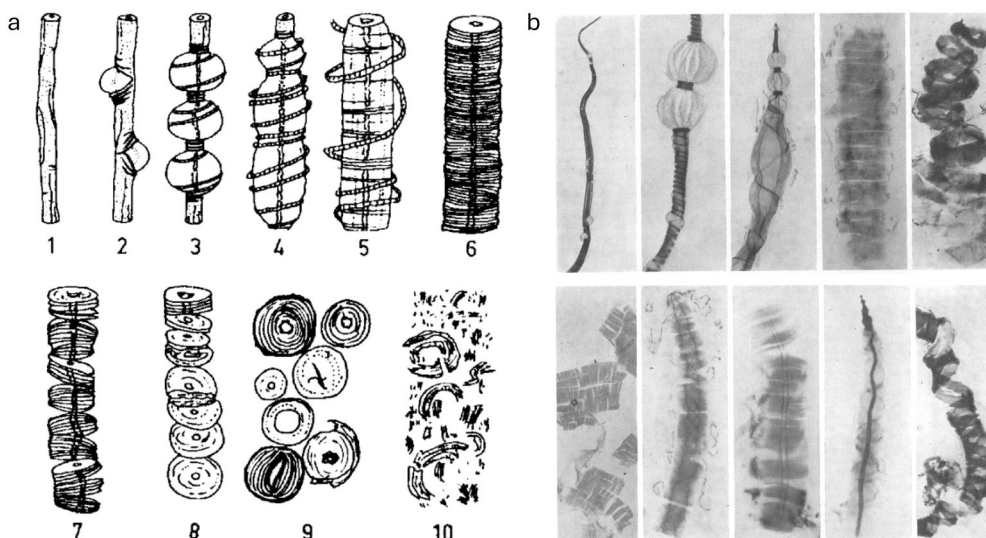


Figure 14. Undissolved fibers in NaCMC solutions. a: classification of fibers in NaCMC solutions by Stawitz and Kage.^[241] b: Optical microscopy images from Ref.^[242]

carboxymethyl cellulose synthesized *via* the slurry process, Feddersen reports that a degree of substitution of $\simeq 0.4$ is required for full solubility in water.^[8] Water-soluble samples with DS as low as 0.2 have been reported.^[250] Nonrandom substitution patterns can significantly alter the critical DS values required for solubility. For example, Liu *et al.*^[251] report that regioselective NaCMC with $x_6 = 0$, $x_2 \simeq (1 - 1.5)x_3$ becomes soluble when the degree of substitution exceeds $DS \simeq 0.3$. On the other hand, CMCs synthesized *via* the induced phase separation approach, which results in high values of χ_0 and χ_3 and a blocky substitution pattern were found to be insoluble up to degrees of substitution as high as 1.2.^[250] The water sorption data in Figure 12 also indicate that Kamide's samples are not soluble up to at least $DS \simeq 0.6$. Solubility of low DS samples can be enhanced by using cellulose solvents such as concentrated NaOH or cadoxen.^[252,253]

Even for a specific starting material and/or reaction protocol, the definition of a solubility threshold is not trivial because different fractions of the cellulose will co-exist in different states. Reports of solubility of NaCMC in water are usually qualitative, and are based on whether the sample appears clear to the eye. While this serves as a good starting point to characterize solubility, quantitative methods should be developed for more detailed analysis of CMC solubility.

Microscopy^[242,254] and filtration tests typically reveal the presence of some insoluble residues for NaCMC samples in the soluble DS range.^[208] GPC experiments reveal similar trends to those observed in Figure 7 but much higher fractions of non-filterable material.^[208,228] Such tests probably overestimate the fraction of insoluble matter. Filtration through $0.1 \mu\text{m}$ pores of a $DS = 1.3$ NaCMC sample has been shown to lead to little or no mass loss.^[255] In addition to insoluble gel particles, a polymer can be *molecularly dissolved* when its chains are well dispersed and solvated, in contrast to

colloidally dissolved, where a large fraction of the chains associate into large aggregates, as discussed in Refs. [67,256–258]

5.1. Undissolved cellulose fibers in CMC solutions

Early microscopy work by Hoppler and Stawitz and Kage established the presence of large, undissolved fibers in solutions of CMC, see Figure 14. They are conjectured to arise from ‘*wood cells that react more slowly during the etherification due to their large dimensions or more dense structure*’. [259] Jardeby *et al.* [254,259,260] later performed more detailed investigations on the influence of the starting cellulose materials and reaction conditions on the resulting fibers. They measured the degree of substitution for several CMC samples and reported values between 0.12 and 0.66. The fiber length distribution, measured by optical microscopy in Refs. [254,260], was found to be polydisperse and peaked at approximately 0.2–2 mm, depending on the sample. The fiber width also showed high dispersity, with a mean value of $\sim 20 \mu\text{m}$.

Based on the above observations, Jardeby *et al.* proposed a general 3-step mechanism of fiber dissolution that depends on the substitution level: At low substitution ($\text{DS} \simeq 0.1$) the fibers remain largely crystalline, which is consistent with the XRD data discussed above. At intermediate substitution ($\text{DS} \simeq 0.3$ to 0.5) the fibers swell and display the ballooned morphology shown in Figure 14a–3. As the substitution increases to $\text{DS} \simeq 0.5$ to 0.6 the swollen fibers convert into gel particles, and at still higher DS a clear solution forms. These gel particles are macroscopic and distinct from the microgel-like aggregates discussed in the following section. Chapter 2 of Ref. [34] contains a more detailed discussion of these studies.

5.2. CMC in the acid form

When excess acid is added directly to a NaCMC solution, the sample becomes turbid. [261] If the acid is subsequently removed by dialysis against deionized water, the resulting HCMC remains in solution and typically shows a slight opalescence. Once it is dried, however, HCMC does not re-dissolve in water, presumably because it remains kinetically trapped in the crystalline solid form. A moderately concentrated alkali solution is required to solubilize it. As with NaCMC, the solubility of HCMC in water increases with increasing degree of substitution.

The degree of substitution of NaCMC is commonly determined by converting the sample to the acid form and performing a potentiometric titration. In the standard approach, the HCMC polymer is dissolved in excess alkali, then back-titrated to $\text{pH} \simeq 8$. [211] The ASTM procedure specifies conversion to the acid form by adding nitric acid and ethanol to the solid NaCMC powder to produce a slurry, followed by repeated washing with deionized water to remove low-molar-mass salts.

Because highly substituted HCMC is partially soluble in water, some of this fraction can be lost during the repeated washing steps of the ASTM procedure, which leads to artificially low measured degrees of substitution. [262] Conversion by addition of excess acid followed by dialysis against deionized water is less likely to remove the highly

substituted material and is therefore preferable to the ethanol/nitric-acid method described in the ASTM standard.

5.3. Solubility of CMC in non-aqueous media and mixed solvents

Commercial grades of NaCMC are insoluble in most common organic solvents, with a few exceptions such as glycerol. Formic acid and some ionic liquids can also dissolve CMC.^[263,264] An early patent^[265] reported that NaCMC with high degree of substitution is soluble in organic solvents but this has not been reproduced to date. Mixtures of water with non-solvents can dissolve NaCMC.^[238] Dissolution can be slow, particularly for viscous solvent mixtures.^[266] Solubility increases with degree of substitution: highly substituted grades ($DS \simeq 1\text{--}1.2$) dissolve readily, whereas weakly substituted grades ($DS \simeq 0.7\text{--}0.9$) tend to form gels, which slows down the dissolution process.^[231,267] As a general rule, NaCMC has higher tolerance for solvents of higher dielectric permittivity, presumably due to the entropy gain upon dissolution from dissociated counterions. NaCMC is more soluble in salt-free media, and can be salted out with added NaCl, especially in water/non-solvent mixtures.^[268]

Figure 15 shows the solubility boundary of NaCMC in water/non-solvent mixtures as a function of polymer concentration. The non-solvent mole fraction required for phase separation decreases with increasing polymer concentration. Even at a modest concentration of 10 g/L ($\simeq 1$ wt%), phase separation occurs at non-solvent mole fractions of only $x_m \simeq 0.2\text{--}0.3$. NaCMC therefore cannot be used in alcohol-rich formulations such as hand sanitizers.

Substituting organic counterions for sodium ones leads to large increases in the solubility of CMC in non-aqueous solvents.^[269,270] A systematic study of the solubility of

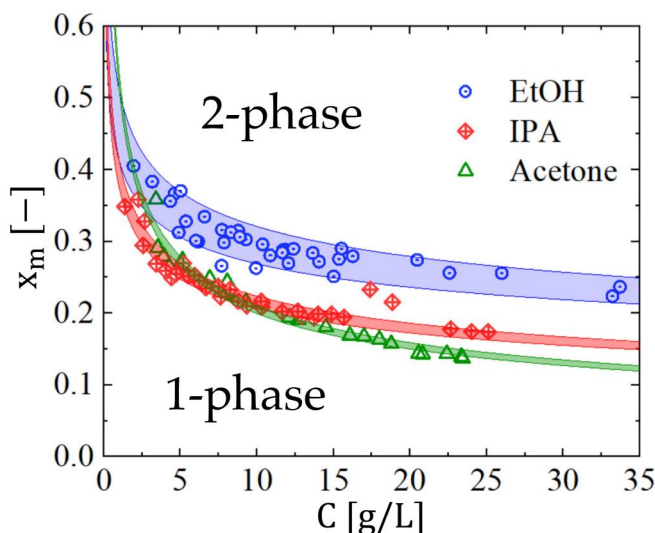


Figure 15. Solubility diagram for NaCMC $DS = 0.97$ and $M_w = 360$ kg/mol in water/ethanol, water/isopropanol and water/acetone mixtures. x_m is the mole fraction of non-solvent at which phase separation happens. Phase boundaries were determined visually from the onset of turbidity when adding a non-solvent to a NaCMC solution in water. Figure adapted from Ref.^[238]

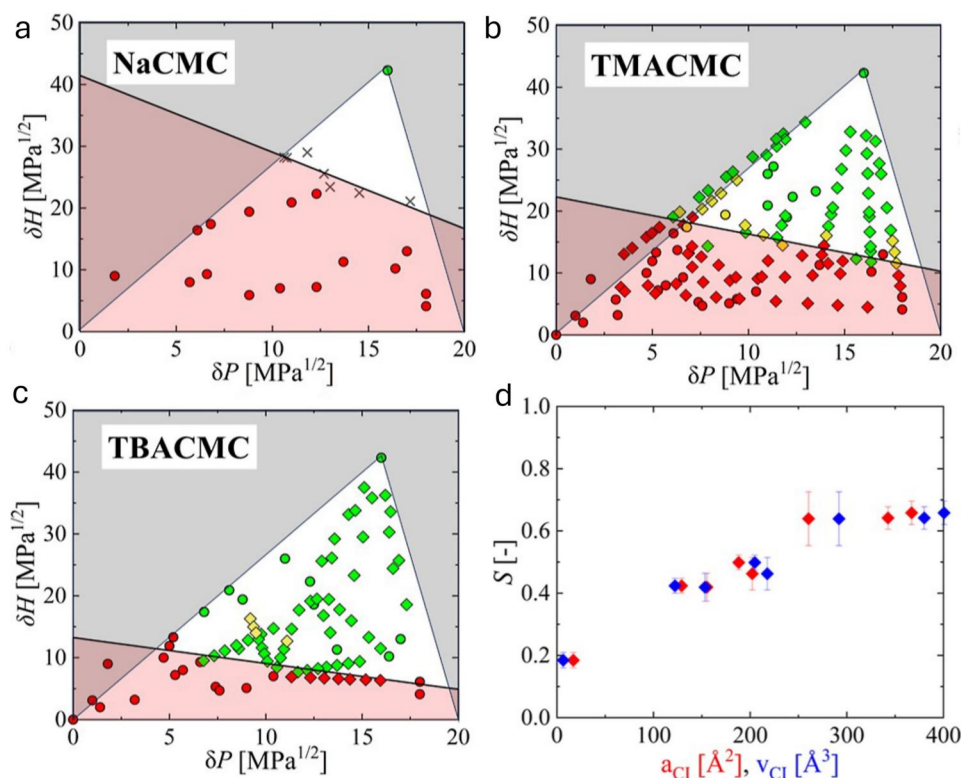


Figure 16. Hansen solubility diagrams for a) sodium, b) tetra-methyl ammonium (TMA) and c) tetra-butylammonium (TBA) salts of CMC. The x- and y-axis are the Hansen polarity and hydrogen bonding solubility parameters respectively. Red symbols indicate non-solvents and green symbols indicate solvents and black crosses the solubility boundary. Water corresponds to the (16,42) point. A triangle is drawn between the origin, (0,20) and the water datum and the ratio of soluble area to the total area is plotted in the d) panel as a function of counterion area (red symbols) and volume (blue symbols) for various counterions. Figure adapted from Ref.^[270]

various salts of CMC was carried out by Hou and coworkers, who showed that Hansen solubility can be used to empirically describe the solubility of CMC polymers in solution, as shown in Figure 16.

In brief, the Hansen approach, developed for nonionic polymers, assigns solvents three solubility parameters: δ_D , δ_P and δ_H , which separate the solvent's cohesive energy into dispersion, polar and hydrogen-bonding interactions. Figure 16a-c plots δ_H against δ_P for some 50 solvents. Most solvents are contained inside a triangle with vertices (0,0), (20,0) and (16,42), with the last point corresponding to (δ_P , δ_H) for water. Solvents located in the top part of the triangle, corresponding to polar and protic media, are able to dissolve CMC, and are indicated by green symbols. Solvents at the bottom part of the triangle, corresponding to apolar, aprotic media do not dissolve CMC and are shown by red points. Solvents that swell but do not dissolve the polymer are shown as yellow symbols.

CMC with organic counterions such as TMA⁺ or TBA⁺ displays greater solubility in organic media than NaCMC, as reflected by the larger area of the Hansen triangle

covered by green symbols. A dimensionless parameter S can be defined that corresponds to the ratio of the soluble region of the Hansen diagram to the total area of the triangle. This is plotted as a function of counterion volume and counterion area on Figure 16d.

6. Dilute-solution conformation and hydrodynamic properties

Solutions below the overlap concentration c^* are in the dilute regime meaning that chains do not interpenetrate.^[62,271] Data in this regime allow extrapolation of physical quantities to the $c \rightarrow 0$ limit, which reflects single chain properties.^[271]

6.1. Static light scattering (SLS)

Static light scattering can be used to measure the radius of gyration of a polyelectrolyte chain in the infinite dilution limit. In contrast to the more common measurement of chain size such as the hydrodynamic (R_H) or viscosimetric (R_η) radii, the radius of gyration is a geometric quantity, which is not influenced by hydrodynamics.

The scattering intensity of a dilute polyelectrolyte solution with excess added salt ($c_s \gg fc/2$, where f is the fraction of monomers with a free counterion, around 0.5 for NaCMC in water^[272–274]) can be described by the Zimm equation:

$$\frac{KC}{\Delta R(q)} = \frac{1}{M_w} \left(1 + \frac{q^2 R_{g,z}^2}{3} \right) + 2A_2 C \quad (6)$$

where C is the concentration in mass per unit volume, M_w the weight-averaged molar mass, $R_{g,z}$ the z -averaged radius of gyration, A_2 the second virial coefficient, ΔR the excess Rayleigh ratio (i.e. the Rayleigh ratio of the solution minus that of the solvent), $q = \frac{4\pi n}{\lambda} \sin(\theta/2)$ is the scattering vector with λ the wavelength of light and K is a contrast factor, given by:

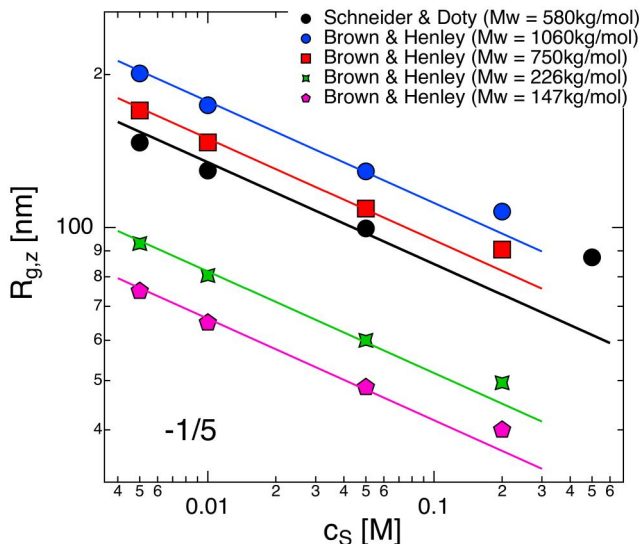
$$K = \frac{4\pi^2 n_0^2}{\lambda^4 N_A} \left(\frac{dn}{dC} \right)_\mu^2 \quad (7)$$

here n_0 is the refractive index of the solvent and dn/dC the refractive index increment. The subscript μ indicates that dn/dC must be measured at constant chemical potential of the salt. In practice, this is done by dialyzing the polyelectrolyte solution against a salt solution, see Refs.^[275,276] for details.

Values of $\frac{dn}{dC}$ have been determined in multiple studies,^[230,255,268,277–285] and are collected in Appendix Table A1 (Appendix A–C). These data do not show any clear trend with DS or added salt concentration. The only measurements of $(dn/dC)_\mu$ for NaCMC have been carried out by Brown *et al.*^[286] and their results are compiled in Table 5. As expected, $(dn/dC)_\mu < dn/dC$. However, other studies^[276] have reported the ratio of $(dn/dC)_\mu$ to dn/dC to increase as the salt concentration increases, which is not observed in Brown *et al.*'s results. Additional measurements of these parameters as a function of added salt concentration and degree of substitution would be very useful to improve the molar mass determination of NaCMC polymers.

Table 5. Refractive index increment of NaCMC in 0.2 M and 0.005 M NaCl. Results in units of mL/g. Data from^[286].

Solvent	Dialysed: $(\frac{dn}{dc})_u$	Non-dialysed: $(\frac{dn}{dc})_u$
0.2 M NaCl	0.132	0.140
0.005 M NaCl	0.136	0.144

**Figure 17.** z-averaged radius of gyration of NaCMC as a function of added salt concentration. Results are data by Brown and coworkers^[233] and Schneider and Doty^[284]. Lines are predicted power-laws of $-1/5$.

6.1.1. Effect of added salt on CMC chain dimensions

Figure 17 plots the radius of gyration of NaCMC with $DS \simeq 1$ as a function of NaCl concentration. Data from Brown and Henley^[233] and from Schneider and Doty^[284] were largely collected outside the $qR_g < 1$ regime where the Zimm approximation is valid, as noted by Davis.^[287] However, the molar masses measured by light scattering for these samples agree with values calculated from the intrinsic viscosities, indicating that their extrapolation to zero scattering angle was carried out correctly despite working at $qR_g > 1$. This outcome is consistent with the fact that Eq. 6 remains accurate for polydisperse Gaussian chains for values of qR_g up to about 2–3.

The radius of gyration decreases with increasing salt concentration following the $R_g \propto c_s^{-1/5}$ dependence predicted by scaling theory for flexible polyelectrolytes.^[288] At high salt concentrations, the datasets deviate systematically above this exponent because the intrinsic chain rigidity limits further contraction as screening increases.^[289] Brown and Henley reported that their samples displayed turbidity at salt concentrations higher than 0.2 M added NaCl, which is not expected for their samples with $DS = 1.06$. Usually such samples are single-phase up to molar concentrations of added NaCl.^[234] Studying the M -dependence of R_g is difficult because the available studies^[233,238,279,284] used polydisperse samples but did not measure the z -averaged molar mass.

In dilute solutions with excess added salt, the radius of gyration of NaCMC chains is expected to scale weakly with the effective charge fraction, $R_g \sim f^{1/5}$.^[288,290]

Since f depends only weakly on DS ^[274] due to counterion condensation,^[291–293] differences in DS should produce only minor changes in chain size.

6.1.2. Persistence length of CMC

The persistence length of polyelectrolytes contains intrinsic and electrostatic contributions.^[294–297] For semiflexible polyelectrolytes such as CMC, the intrinsic term dominates once the added salt concentration exceeds roughly 0.1 M.^[298] Hoogendam *et al.*^[230] analyzed NaCMC chain dimensions using size exclusion chromatography and fitted the R_g – M data to the expanded wormlike chain model, obtaining an intrinsic persistence length of $l_{p,0} \simeq 15$ nm. By contrast, Lopez's analysis of intrinsic viscosity data also using the expanded worm-like chain model^[299] found a smaller value of $l_{p,0} \simeq 5$ nm.^[300] For other polymers, persistence length estimates obtained from radius of gyration, hydrodynamic radius and intrinsic viscosity typically agree to within $\simeq 10\%$.^[301–305] The light scattering data of Brown and Henley, Schneider and Doty, Hou *et al.*^[238] and Yoshida *et al.*^[279] are all incompatible with the value obtained by Hoogendam *et al.*^[306] It may be tempting to discard the data of Hoogendam *et al.*, but these align closely with the R_g – M results of Barba *et al.*^[208] and Shakun *et al.*,^[283] also obtained by GPC coupled with light scattering. Thus, there are two internally consistent sets of results: 1) GPC-LS measurements and 2) standard SLS and intrinsic viscosity measurements, which imply markedly different persistence lengths for CMC.

The discrepancy between these sets of studies remains unresolved and should be addressed in future work. Determining the persistence length of polyelectrolytes is difficult, and there is no clear agreement in the literature on the most appropriate procedure. In our view, the most reliable approach is to measure R_g , $[\eta]$ and the diffusion coefficient for a series of relatively monodisperse polymers at varying salt concentration, and to fit the expanded wormlike chain model to these three quantities.^[298,307–309] This approach was used by Norisuye and coworkers for sodium hyaluronate,^[289,310–312] and comparable datasets for NaCMC would allow the persistence length discrepancy to be resolved.

Alternatively, if the theta salt concentration, that is the added salt concentration^[287] at which $A_2 = 0$, of NaCMC is determined, this would allow for a more direct evaluation of the persistence length of CMC. Note that the theta salt concentration is expected to depend on the added salt type,^[313] the degree of substitution of the chain,^[314,315] and possibly the substitution pattern. Studies on the second virial coefficient of NaCMC show that the second virial coefficient remains positive up to at least 0.5–1 M added NaCl.^[284,316–318]

6.2. Intrinsic viscosity and dilute-solution viscometry

At c^* the viscosity is about twice that of the solvent ($\eta_{sp} \simeq 1$).^[319–321] The overlap concentration is reached when the 'self concentration' of a chain matches the solution concentration,

$$c^* \simeq \frac{N}{R^3}, \quad (8)$$

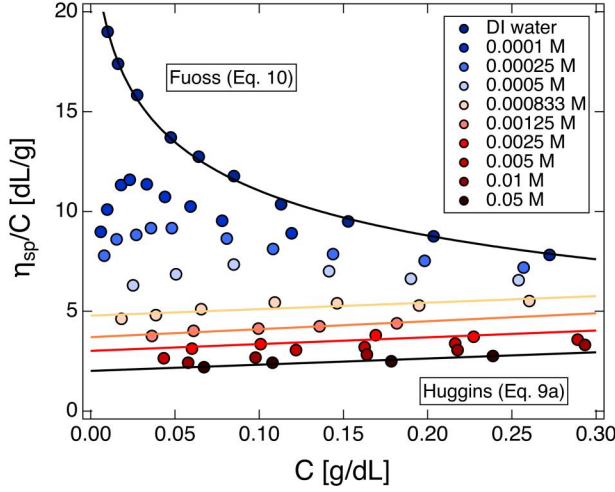


Figure 18. Reduced viscosity of NaCMC as a function of concentration in DI water and NaCl solutions. Data from Ref.^[323], see Ref.^[324] for correct labels. Curves are fits to the Huggins and Fuoss equations (Eqs. 9a and 10).

where N is the degree of polymerization and R the end-to-end distance, so that R^3 represents the pervaded volume of a chain. Added salt screens the electrostatic interactions reducing R along with the corresponding increase in c^* . The overlap concentration can be experimentally measured as the reciprocal of the intrinsic viscosity $[\eta]$.^[322]

In excess salt, that is when the concentration of salt ions ($2c_s$) is much larger than that of free counterions fc , the viscosity follows the Huggins and Kraemer equations:

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c, \quad (9a)$$

$$\ln(\eta_{rel})/c = [\eta] - k_K[\eta]^2 c. \quad (9b)$$

where k_H and k_K are the Huggins and Kraemer's coefficients and $k_H + k_K = 1/2$. Eq. 9 should generally be applied for $c \lesssim [\eta]^{-1}$, corresponding to $\eta_{sp} \lesssim 1.3 - 1.5$ (Figure 18). Hydrophobic moieties on the polymer cause a strong concentration-dependence of the dilute solution viscosity and limit the concentration range of both equations, particularly the Huggins equation, see Refs.^[325–327] for details. For sufficiently dilute solutions, both equations apply.

In low salt solutions ($2c_s \ll fc$), the reduced viscosity increases upon dilution (Figure 18) due to chain expansion, inter-chain repulsion, and ionic friction.^[298] Fuoss^[328,329] proposed the empirical form:

$$\frac{\eta_{sp}}{c} = \frac{A}{1 + B'c^{1/2}}, \quad (10)$$

where A corresponds to $\lim_{c \rightarrow 0} \eta_{red}$ and B' correlates with the effective chain charge.^[330] A c -independent term is sometimes added to the RHS of Eq. 10. Equation 10 overestimates $[\eta]$ because a viscosity maximum appears at sufficiently low concentrations, first noted by Inagaki *et al.*^[323] The maximum occurs when $2c_s$ becomes comparable to the free counterion concentration fc .^[298] For NaCMC in aqueous solution, there is roughly one free counterion per two monomers,^[238,273,274,331] so in DI water ($c_s \simeq 4 \times 10^{-6}$ M

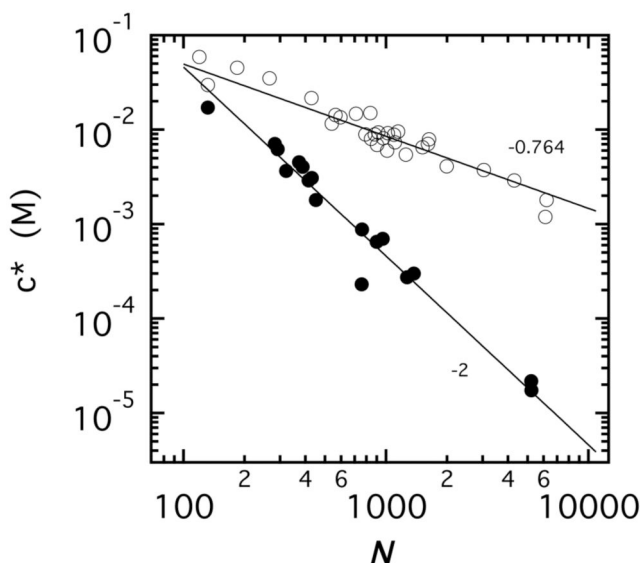


Figure 19. Overlap concentration of CMC as a function of degree of polymerization N in DI water and 0.1 M aqueous NaCl. In DI water, the overlap concentration is obtained from the $\eta_{sp}(c^*)$ criterion. In excess salt, c^* is estimated as the reciprocal of the intrinsic viscosity. Lines are power-laws with theoretical exponents^[288] for polyelectrolytes in salt-free and excess salt regimes. Figure reproduced from Ref.^[300], with data from Refs.^[12,67,201,208,234,237,277,280,284,286,343–350] see also^[234] for selection of data.

from dissolved CO_2) the maximum appears near $c_{\max} \simeq 10^{-5}$ M ($\simeq 2.5 \times 10^{-3}$ g/L). Below $c_{\max}$ it is difficult to obtain accurate measurements of η_{red} , making extrapolation to $c = 0$ unreliable.

The use of Fedors or Wolf equations^[332,333] to evaluate the intrinsic viscosity of NaCMC^[232,334] in salt-free or low salt solvents is not recommended as they do not correctly capture the concentration dependence of the specific viscosity at low concentrations.^[298,335]

Figure 19 shows the overlap concentration of CMC in salt-free water and in 0.1 M NaCl as a function of degree of polymerization. In DI water, which contains only $\simeq 4 \times 10^{-6}$ M residual salt from carbonic acid,^[238,336–338] electrostatic interactions remain long-ranged in the dilute regime and chains adopt rod-like conformations.^[62,339] This gives $R \propto N$ and $c^* \propto N^{-2}$.^[298] In 0.1 M NaCl, electrostatics are short-ranged and act similarly to excluded volume in neutral polymers, leading to $R \propto N^{0.59}$ and $c^* \propto N^{-0.78}$, in agreement with observations for other polyelectrolytes.^[301,340–342] Mark-Houwink-Sakurada relationships, obtained from a compilation of literature data,^[234] are listed in Table 6.

Note that for $N \simeq 100$, the excess salt and salt-free curves intersect, possibly corresponding to the point at which the CMC chain is not perturbed by electrostatic interactions, i.e. the electrostatic blob.^[62,351,352]

6.3. Shear-rate artifacts in capillary viscometry of CMC

Ordinary capillary viscometers impose shear rates of order 10^3 s^{-1} . For low-salt and high-molar-mass NaCMC, these conditions fall in the non-Newtonian regime, and

Table 6. MHS relations for the intrinsic viscosity of NaCMC in DI water and in NaCl solutions: $[\eta] = K_{\eta} N^a$, where $[\eta]$ is in units of M^{-1} .

solvent	K_{η}	a
DI water	0.00015	2.5
0.01 M	0.81	0.82
0.1 M	0.29	0.87

For DI water, $[\eta]$ is estimated as $1/c^*$, where c^* is the point at which $\eta_{sp} = 1$.

shear-dilution viscometers are required to measure the viscosity as a function of shear rate. This limitation has been noted repeatedly in the polyelectrolyte literature for decades,^[234,298,319,330,342,343,353–355] but viscometry studies on polyelectrolytes often overlook it, with some studies implausibly claiming that capillary viscosimetry data for high molar mass samples are not influenced by shear thinning.^[334] Coupled with the lack of adequate determination of the molar mass, this renders a significant number of viscosimetry studies unreliable. A survey of the literature, indicating which measurements are affected, is given in the supplementary information of ref. [234].

7. Molecular solubility and supramolecular aggregation

Significant discussion in the literature has taken place on the question of whether carboxymethyl cellulose in aqueous solution is dissolved at a *molecular* or *colloidal* level, with many apparently contradictory results.^[63,67,356] Here, we restrict our discussion to dilute solutions, where chains do not overlap. Following the scheme of Burchard and coworkers,^[256] molecular dissolution corresponds to a state where chains are individually dispersed and well-solvated. Colloidal dissolution corresponds to when most chains are aggregated into multi-chain clusters. It is often the case that a fraction of the polymer is molecularly dissolved while the rest is aggregated. This can be especially pronounced for polymers like CMC, where the second order heterogeneity in chemical composition results in chains with varying tendencies to aggregate.

7.1. Experimental evidence for molecular solubility

Many osmotic pressure^[316–318,357–359] and light scattering^[238,279,284,286,360] studies for NaCMC with $0.45 \leq \text{D.S.} \leq 1.7$ in excess salt solutions show positive second virial coefficients and molecular weights matching those of single chains. These features are characteristic of molecularly dissolved polymers. The variation of intrinsic viscosity^[234,300] and radii of gyration (R_g)^[230,233,283,361] with degree of polymerization and salt concentration, discussed above, are also typical of semiflexible polymers in good solvents. Light scattering experiments are usually performed after filtration and/or centrifugation to remove dust particles. These procedures can also lead to the removal of aggregates. As we have seen in sec. 4.2, the mass loss upon filtration for $\text{DS} \geq 0.9$ is small (less than 1%), meaning that the well-dispersed fraction measured by light scattering corresponds to the majority of chains. Such results are also consistent with SANS and SAXS data on semidilute solutions, which show behavior typical of well dispersed chains.^[12,67,238,362,363]

7.2. Experimental evidence for aggregation

Four types of supramolecular structures have been observed for NaCMC; we classify them as follows:

- I. Regions of unreacted or weakly reacted cellulose present in NaCMC form large fibers,^[259,260,282] easily removed by filtration and/or centrifugation, see the discussion above. These aggregates are found for low DS samples and can be dissolved by addition of NaOH.^[253]
- II. Smaller aggregates, typically sub-micron, have also been observed by light scattering,^[268,364] AFM^[365] and SANS.^[67,366] These aggregates are probably not of a unique kind but may rather correspond to different aggregation mechanisms depending on D.S., salt concentration etc. A possible structure is that of the fringed micelle,^[65,365,367,368] which is supported by the AFM^[365] data on dried NaCMC and by the GPC-light scattering results of Kötzt *et al.*^[361] which show $R_g \sim M_w^0 \simeq 53$ nm (see Figure 21). This variation is characteristic of elongated objects undergoing lateral aggregation.^[256,369,370] Given that several light scattering studies^[230,283,284,286,360] on NaCMC with D.S. in the range of 0.7–1.1 report no aggregation for filtered and/or centrifuged aqueous salt solutions, it seems likely that if these aggregates are common, they are at least in part removable by filtration/centrifugation and/or addition of salt.
- III. Liebert *et al.*^[365] report the formation of large network structures upon solution drying for NaCMC samples with nonrandom substitution. Gel formation in concentrated solutions has been observed in many other studies.^[10,13,65,208,371]
- IV. Polyelectrolytes in salt-free or low salt solutions are known to display a slow mode in their DLS autocorrelation function. While the precise mechanism driving this kind of aggregation remains unclear,^[298] the strong sensitivity of aggregates to added salt concentration establishes that this kind of assembly is electrostatically driven. No systematic study on the characteristics of this kind of aggregation has been performed for NaCMC. The slow mode observed by dynamic light scattering by Lopez and Richtering^[237] and Behra *et al.*^[277] in salt-free solution likely contains a contribution from these and type II aggregates.

7.2.1. Fringed micelles

For cellulose derivatives, intermolecular clusters are usually thought to form ‘fringed micelles’. Possible structures for these fringed micelles are shown in Figure 20. The common feature is the presence of segments of unsubstituted cellulose, which form a crystalline core out of which dangling chains emanate. A detailed mathematical treatment of the scattering properties of the fringed micelle was developed by Burchard.^[368] In practice, accurate fitting of a form factor to scattering data is difficult, but the basic features of the model can be elucidated. As we will see below, experimental evidence favors the structures schematized in panels d of Figure 20.

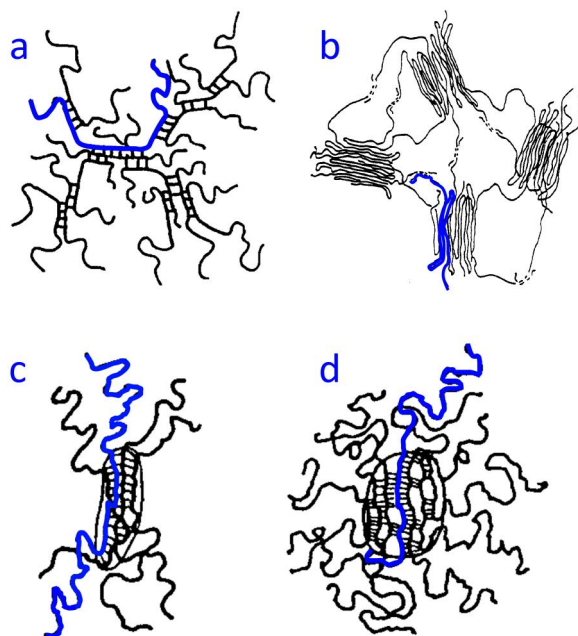


Figure 20. Possible structures of fringed micelles. Sections where chains are aligned in parallel are the crystalline cores. Schematics are adapted from Refs. [256,369,372]. Blue lines are single chains within a multi-chain aggregate.

7.2.2. Experimental evidence for fringed-micelle aggregates

While most published light scattering studies are consistent with NaCMC being molecularly soluble, a few studies give evidence supporting strong inter-molecular aggregation. Figure 21 plots the radius of gyration of CMC solutions where aggregation is apparent. Burchard *et al.*^[369,372] and Sitaramaiah and Goring^[268,373] (SG) performed static light scattering on solutions of NaCMC in 0.1 M NaCl for samples of varying molar mass.^[374] SG's samples have DS $\simeq 0.62 - 0.74$, Burchard *et al.* do not report the DS of their polymers. Both datasets display a scaling relationship of $R_{g,z} \propto M_w^{1/3}$ as expected for compact objects (fractal dimension $d_F = 3$) with constant polydispersity.^[375] The $1/3$ exponent contrasts with the larger values observed for CMC in samples of higher degree of substitution.

The molar mass measured by SG using static light scattering was found to be $\simeq \times 4$ larger than the molar mass calculated from the intrinsic viscosities in 0.1 M NaCl using the MHS relationship reported in Ref.^[372] or from their sedimentation-diffusion estimates. This difference persisted despite extensive centrifugation of their samples. The results suggest the coexistence of a fraction of chains which are molecularly dissolved, and a fraction which is highly aggregated. The aggregated fraction makes a large contribution to M_w and $R_{g,z}$ but not to the intrinsic viscosity because their compact size results in a low hydrodynamic volume relative to their mass ($[\eta] \propto R_H^3/M_w$, where R_H^3 is the hydrodynamic volume of the chain). The M -dependence for the diffusion coefficient, intrinsic viscosity, and sedimentation coefficient in SG's study is also consistent with the scaling relationships observed for molecularly dissolved

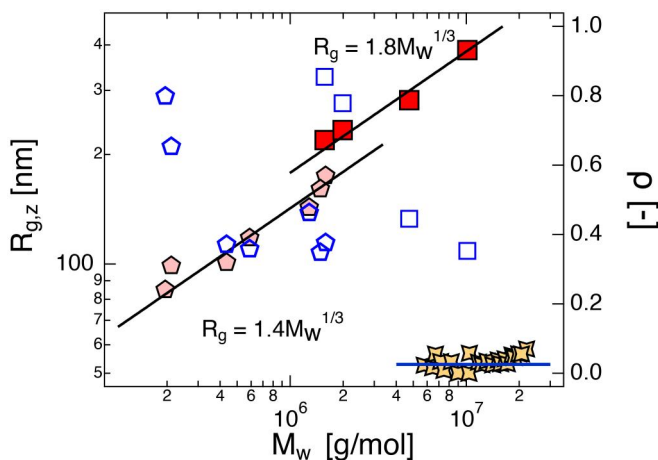


Figure 21. Light scattering results on fringed micelles. Red/Orange symbols are radius of gyration: Data are by Burchard *et al.* (DS not given) in 0.1 M NaCl (red squares), Sitaramaiah and Goring for DS = 0.62–0.74 in 0.1 M NaCl (pentagons) and Kotz *et al.* (stars, measured by SEC). Black lines are power-laws with exponents forced to 1/3, as expected for compact objects. Blue line is $R_g = 53$ nm. Blue hollow symbols are $\rho = R_g/R_H$. R_H for Sitaramaiah and Goring's samples was estimated from the intrinsic viscosity, and therefore corresponds to the hydrodynamic radii of a single chain and not of an aggregate, see the text for details.

polymers in good solvent,^[298,376] indicating the aggregates do not strongly contribute to these quantities.

Further evidence supporting the fringed micelle structures in Figure 20 comes from the dimensionless ratio ρ reported by Burchard *et al.* Polyelectrolytes in excess salt or polydisperse polymers in good solvent typically display $\rho \simeq 1.5 - 2$. For compact spheres $\rho = 0.78$. Burchard *et al.*'s data at high M_w display values of $\rho \simeq 0.4$, below those of hard spheres, which are characteristic of objects with a dense core and dangling chains such as heterogeneously cross-linked microgels.^[377–379]

Following the preceding discussion, we assume that the intrinsic viscosity of SG's samples contains a negligible contribution from aggregates. The universal ratio $U_{\eta,f}$ is given by:

$$U_{\eta,f} = 1/6\pi \left(\frac{[\eta]M}{N_A R_H^3} \right)^{1/3} \quad (11)$$

where $[\eta]$ is the intrinsic viscosity, R_H the hydrodynamic radius, M the molar mass, and N_A Avogadro's constant.

$U_{\eta,f}$ is known to take a value of $\simeq 0.12$ for polymers in solution.^[298] Using the intrinsic viscosity values given in Refs.^[268,373], the hydrodynamic radius of individual chains is calculated, see Table 7. Furthermore, assuming a value of $\rho = 2$ for well dispersed chains, $R_{g,z}$ for a single chain is estimated. These values are listed as R_g^* in Table 7. Then, taking the light scattering radius of gyration to correspond to that of the fringed micelle,^[380] we estimate the ratio of the R_g of the multi-chain aggregate to that of a single chain, and find values of $\sigma^* \simeq 2-4$ for SG's samples, where σ^* is the ratio of

Table 7. Measured and calculated parameters for Sitaramaiah and Goring's samples.

Sample	DS [-]	N_w^{LS} [-]	$R_{g,z}^{LS}$ [nm]	$[\eta]_{0.1M}$ [M ⁻¹]	N_η [-]	R_H^* [nm]	R_g^* [nm]	$\sigma^* = R_{g,z}^{LS}/R_g^*$ [-]
H1	0.66	7460	175	262	2500	45	91	1.9
H2	0.62	7070	161	256	2430	45	89	1.8
H3	0.63	2790	118	160	1420	32	64	1.8
M1	0.72	5880	143	151	1330	31	61	2.3
M2	0.72	2000	101	127	1080	27	54	1.9
L1	0.7	3700	—	111	935	25	49	—
L2	0.74	960	99	56.3	427	15	30	3.3
L3	0.73	890	85	34.3	241	11	21	4

N_w^{LS} and $R_{g,z}^{LS}$ are the weight averaged degree of polymerization and z-averaged radius of gyration measured by SLS. $[\eta]_{0.1M}$ is the intrinsic viscosity measured in 0.1 M NaCl and N_η is the degree of polymerization calculated using the MHS relationship reported in^[372]. R_H^* is the hydrodynamic radius of a single chain estimated from Eq. 11 and the measured intrinsic viscosities, and R_g^* is the radius of gyration of a single chain calculated as $R_g^* = \rho R_H^*$ with $\rho = 2$. The parameter σ^* is an estimate of the ratio of the radius of gyration of the fringed micelle to that of a single chain.

the radius of gyration of a fringed micelle to that of an individual chain. Noting that our coarse estimates for σ^* are likely underestimates, we judge they support the structures sketched in panels a and d of Figure 20.

The size exclusion chromatography data of Kotz *et al.*,^[361] plotted in Figure 21 show $R_g \sim M_w^0 \simeq 53$ nm. Unlike the data from Refs.^[268,369,372,373], each point here corresponds to a monodisperse fraction of aggregates, with no contribution from the molecularly dispersed chains, which elute at earlier times and show $R_g \sim M_w^{1/2}$ (see Figure 3 of Ref.^[361]). The unusual independence of R_g on molar mass is consistent with laterally aggregated chains, where the molar mass increases proportionally with the number of chains in the cluster, but the longest dimension of the aggregate is largely unchanged. This supports the pictures in panels c and d of Figure 20.

In summary, the data of Burchard *et al.* and Sitaramaiah and Goring are broadly consistent with the fringed micelle model. Though the specific structure of the micelles cannot be resolved in any detail, the experimental evidence is most consistent with structures d of Figure 20. A more quantitative evaluation of the fringed micelle model is not possible from the present data.

7.2.3. Atomic force microscopy of CMC aggregates

Representative examples of type II and type III aggregates obtained by atomic force microscopy are shown in Figure 22. The microscopy work on these types of aggregates is more sparse than for type I aggregates and no systematic studies have been performed to clearly distinguish the effect of different parameters (salt concentration, temperature, pH, etc.) on aggregate formation. Further, it is not known if the observed structures are thermodynamically stable or whether they correspond to kinetically trapped assemblies. So far, the best evidence for fringed-micelle structures comes from the light scattering work discussed above.

7.3. The slow mode and low- q upturn

Long-ranged inhomogeneities are commonly reported in polyelectrolyte solutions,^[382–385] even though their existence is difficult to reconcile with the high osmotic pressure and correspondingly low osmotic compressibility of salt-free systems, which is

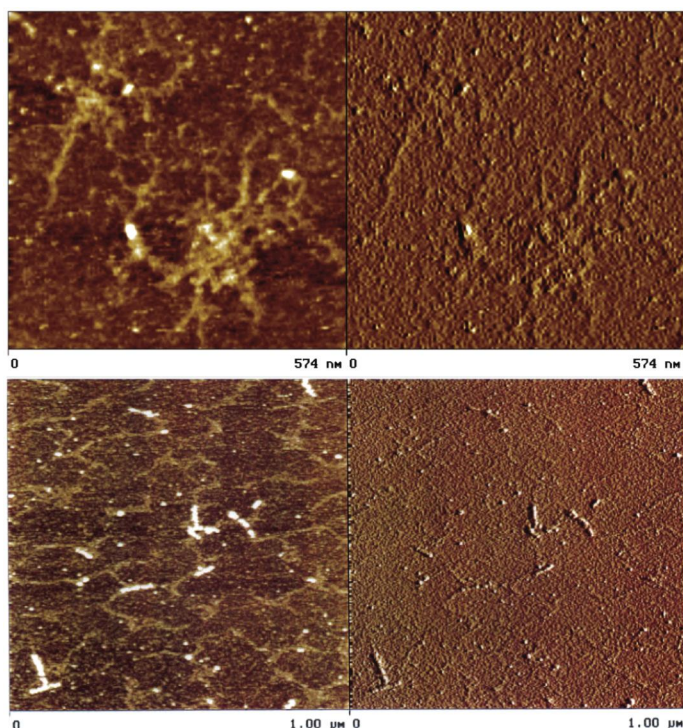


Figure 22. AFM images of CMC supramolecular assemblies. Top panels: fringed-micelle-like aggregates observed by Liebert et al., from reference [365]. Bottom: Type III aggregates, also Liebert et al.

expected to suppress such inhomogeneities.^[288,386] Dynamic light scattering often reveals a slow relaxation mode, and small angle scattering profiles frequently display a low- q upturn, both features suggesting fluctuations or structures on length scales of hundreds of nanometers. These observations are therefore surprising from a theoretical standpoint and remain the subject of debate.^[298,385,387]

Carboxymethyl cellulose solutions exhibit the same behavior. Dynamic light scattering measurements on several NaCMC salts^[237,277,282] show a pronounced slow mode whose apparent size depends on the pore size used during filtration. Changes that occur within a week of filtration indicate that the relevant structures are not at equilibrium, consistent with findings for polystyrene sulfonate.^[388] Small angle neutron scattering data likewise reveal large-scale inhomogeneities in CMC solutions.^[12,67,363,389]

Because multiple types of aggregates are present in typical CMC samples, it is difficult to attribute the slow DLS mode and the low- q excess scattering solely to these long-ranged ‘polyelectrolyte inhomogeneities’. The overlap between different populations obscures the origin of these signals and complicates interpretation.

The main characteristics of each type of aggregate for the classification proposed here, along with key experimental observations are summarized in Table 8.

Table 8. Proposed classification of supramolecular aggregates in solutions of NaCMC. * excluding non-gelling fraction of sample.

Type	Proposed structure	Formation mechanism	Size range	Key influencing factors	Experimental criteria
I	Macroscopic cellulose-rich fibers or residues	Unreacted cellulose	Large, optically visible or micron-scale fibers	Present only for low DS	Observable by microscopy, can be dissolved by addition of concentrated NaOH.
II	Supramolecular aggregates, possibly fringed micelles	Unsubstituted cellulose regions of individual chains associate to form a crystalline core from which dangling chains emanate	10s-100s nm	inhomogeneous substitution	Detected by SLS, DLS, AFM, SEC-MALS. The molar mass and radius of gyration from LS exceed values inferred from intrinsic viscosity or sedimentation. Compact-object scaling such as $R_g \sim M_w^{1/3}$ or $R_g \propto M_w^0$.
III	Large network structures or gels	Intermolecular associations between unsubstituted patches of cellulose form a transient network	Entire size of sample*	Heterogeneous substitution, high concentration (usually above entanglement point)	Inferred from oscillatory rheology data showing gel formation. Only a few observations by microscopy. Not present at high pH when cellulose is solubilized.
IV	Unknown	Presently not understood, likely electrostatic in origin	static size ~ 100 nm	Salt concentration, filtration procedure	Identified by a slow relaxation mode in DLS and/or a low- q upturn in SANS/SAXS; can be removed by filtration ^[381]

8. Rheological properties of carboxymethyl cellulose solutions and gels

Here we briefly review the main rheological phenomena and discuss them in the context of the structural picture developed above. A more detailed review of the flow properties of CMC will be presented elsewhere. Polyelectrolyte rheology in general features many open questions^[320,390,391] which will not be discussed here; we limit our discussion to the general properties of CMC without comparison to specific theoretical models.

Highly substituted samples, typically with $DS \geq 1$, are molecularly dissolved and have rheological properties similar to those of other hydrophilic, semiflexible polyelectrolytes.^[67,201,279,344–346] Weakly substituted samples, typically with $DS \leq 1$, contain unsubstituted cellulose-rich sequences that promote inter-chain attraction. These associations lead to associative solution rheology above the entanglement concentration and, at sufficiently high concentrations, weak gel formation.^[12,208,371] The cross-over between high

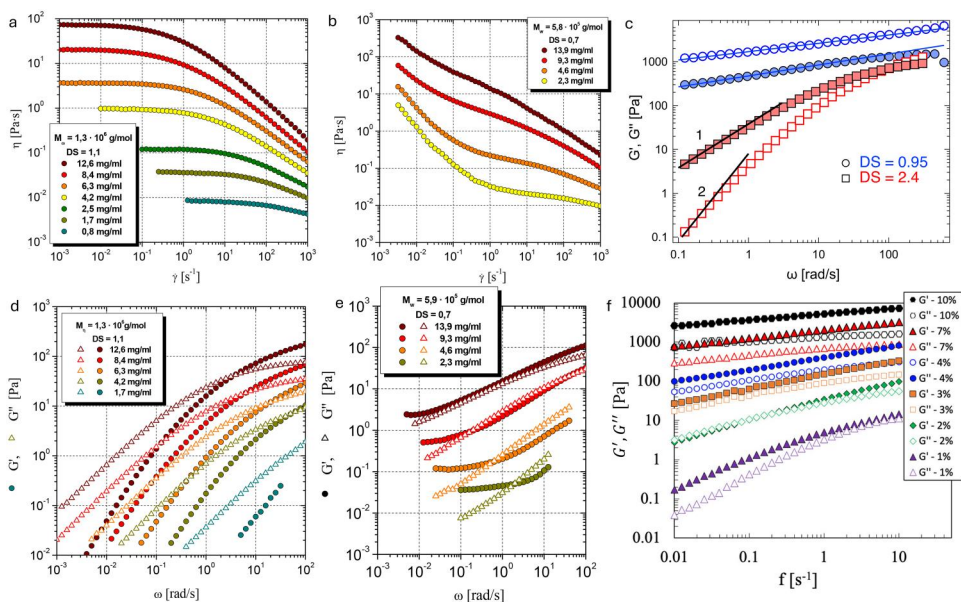


Figure 23. Rheological properties of NaCMC with different degrees of substitution. (a, b) Apparent viscosity as a function of shear rate ($\dot{\gamma}$) for NaCMC with (a) DS = 1.1 and (b) DS = 0.7 in 0.1 M NaNO₃ with 200 ppm NaN₃. (d, e) Storage and loss moduli as a function of angular frequency for NaCMC with (d) DS = 1.1 and (e) DS = 0.7 in 0.1 M NaNO₃ with 200 ppm NaN₃, same samples as in parts a-b. (c) Oscillatory shear response of NaCMC with DS = 0.95 and DS = 2.4 at 100 g/L in 0.1 M NaCl. (f) Concentration dependence of the linear viscoelastic response of weakly substituted NaCMC in DI water. Figure adapted from Refs. ^[13,208,347]

and low DS depends on the substitution pattern, which is dictated by the synthesis conditions.

Figure 23a-b and 23d-e compare the steady and oscillatory shear response of highly and weakly substituted NaCMC in 0.1 M salt solutions. For the high-DS sample, the steady shear flow curves show a Newtonian plateau at low shear rates followed by shear thinning at high shear rates. The cross-over between these regimes can be described by the Carreau model at low concentrations and by the generalized Carreau-Yasuda model at higher concentrations.^[12,67,392,393] The oscillatory shear data show the terminal response expected for entangled polymer solutions, with $G' \propto \omega^2$ and $G'' \propto \omega$ at low frequencies, followed by a cross-over at higher frequencies.^[320]

The DS = 0.7 sample, shown in Figure 23b and 23e, differs sharply from the more substituted sample. At low shear rates, the apparent viscosity does not reach a Newtonian plateau but instead increases continuously as the shear rate decreases. The oscillatory shear data show a low-frequency plateau in G' , consistent with incipient weak gel formation. The transition between solution and gel behavior likely depends on the substitution pattern, but this dependence has not been studied systematically.

The transition between solution and weak gel is illustrated in Figure 23c, which compares the oscillatory shear response of NaCMC with DS = 0.95 and of the same polymer after further etherification to DS = 2.4. Both samples were measured at 100 g/L in 0.1 M aqueous NaCl. As in Figure 23a-b, the highly substituted sample shows liquid-like behavior characteristic of entangled polymer solutions. By contrast, the less substituted

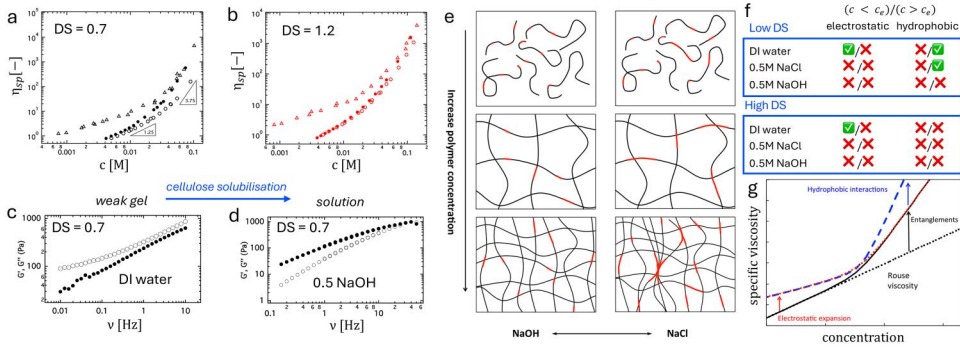


Figure 24. (a, b) Specific viscosity as a function of polymer concentration for NaCMC with (a) DS = 0.7 and (b) DS = 1.2 in DI water (triangles), 0.5 M NaCl (filled circles) and 0.5 M NaOH (hollow circles). (c, d) Oscillatory shear response of DS = 0.7 NaCMC at high concentration in (c) DI water and (d) 0.5 M NaOH, showing the transition from weak gel to solution-like behavior upon cellulose solubilization. Hollow symbols are storage modulus (G') and filled symbols are loss modulus (G''). (e) Schematic representation of the structure of NaCMC solutions in NaOH and NaCl for different polymer concentration regimes. Red segments represent unsubstituted cellulose-rich sequences. (f) Contributions of electrostatic and associative interactions for weakly and highly substituted samples in different aqueous media. (g) Schematic contribution of electrostatic expansion, entanglements and associative interactions to the concentration dependence of the specific viscosity. Adapted from Ref.^[12]

sample displays weakly frequency-dependent moduli, $G' \sim G'' \sim \omega^{0.33}$, characteristic of physically cross-linked gels.

The concentration dependence of the oscillatory shear response of a weakly substituted NaCMC (DS $\simeq$ 0.7) in DI water is shown in Figure 23f. At the lowest concentrations, the samples show associative solution behavior but do not qualify as gels.^[13] Near $c \simeq 3$ wt%, G' and G'' have nearly identical frequency dependences, corresponding to the critical gelation concentration according to the Winter-Chambon criterion.^[394] Above this concentration, the low-frequency storage modulus scales approximately as $G' \sim c^3$, as observed for several samples with different substitution patterns.^[13] The frequency dependence of both G' and G'' weakens with increasing concentration, indicating the formation of a more developed network.

The use of different electrolytes to selectively tune electrostatic and associative interactions provides insight into the rheology of NaCMC solutions. Figure 24a-b compares the viscosity of NaCMC with DS = 0.7 and DS = 1.2 in DI water, 0.5 M NaCl, and 0.5 M NaOH. At low concentrations, where chains are strongly expanded by electrostatic interactions, salt-free solutions are more viscous than solutions with excess added electrolyte.^[320,395] For $c \gtrsim 0.05$ M, however, the viscosities in DI water and 0.5 M NaCl become nearly identical, indicating that electrostatic interactions make only a small contribution to the rheology of concentrated solutions.

Comparison of the viscosities in 0.5 M NaCl and 0.5 M NaOH separates the effect of associative interactions from that of electrostatic screening. Both electrolytes screen electrostatic interactions to a similar extent, but NaOH solubilizes unsubstituted cellulose segments whereas NaCl does not. For the DS = 0.7 sample, the viscosities in NaOH and NaCl solutions are nearly identical below the entanglement concentration ($\simeq 0.03$ M), showing that associative interactions have little effect in dilute and non-entangled

solutions. In well-entangled solutions, by contrast, the viscosity in NaOH is much lower than in NaCl, consistent with the suppression of inter-chain associations in NaOH. For the $DS = 1.2$ sample, the viscosities in 0.5 M NaCl and 0.5 M NaOH remain similar over the measured concentration range, consistent with weaker associative interactions for highly substituted samples. The transition from weak gel behavior in DI water to solution-like behavior in 0.5 M NaOH for $DS = 0.7$ NaCMC is shown in Figure 24c-d. The corresponding molecular picture is shown in Figure 24e, and the separate contributions of associative and electrostatic interactions to the solution viscosity are summarized in Figure 24f-g.

Thixotropic behavior in weakly substituted NaCMC is widely reported in commercial brochures, but has been observed in only a few academic studies.^[396] The available data do not resolve whether gelation and thixotropy arise primarily from long-lived inter-chain associations between unsubstituted cellulose-rich sequences, from large supramolecular aggregates, or from a combination of both. Gel formation may be explained by a transient associative network, whereas thixotropy may require larger aggregates that break down under shear and reform after flow cessation.^[397,398]

9. Conclusions

9.1. Solubility, conformation and supramolecular aggregation

The solution behavior of CMC depends not only on the average degree of substitution, but also on the substitution pattern, i.e. how substituents are distributed between and along the chains. When the substitution pattern is relatively homogeneous, the chains are molecularly dispersed and behave as hydrophilic polyelectrolytes. This is generally the case for commercial samples with $DS \geq 1$, because higher substitution suppresses long unsubstituted patches. As the average DS is lowered, most chains remain relatively uniformly substituted, but a fraction contains blocks of unsubstituted cellulose. In dilute solution, these regions promote inter-chain association and the formation of multichain aggregates. The available data cannot be used to fully resolve their structure, but are consistent with fringed micelles consisting of cellulose-rich crystalline cores from which solvated CMC chains emanate. This structural heterogeneity provides an explanation for the different rheological behavior of weakly and highly substituted samples.

The available osmotic pressure, scattering, viscometry and separation data indicate that most chains in water-soluble CMC samples are molecularly dissolved, while a smaller fraction is present in supramolecular aggregates. Because these aggregates make a disproportionate contribution to static light scattering, even a small aggregated fraction can lead to overestimation of the molar mass and chain dimensions. The observed values of R_g/R_H , the approximate relation $R_{g,z} \propto M_w^{1/3}$ and the discrepancies between molar masses obtained from static light scattering and intrinsic viscosity are consistent with compact multichain aggregates. It remains unclear to what extent these aggregates contribute to the slow relaxation mode observed by dynamic light scattering and the low- q upturn observed by small-angle scattering.

For the molecularly dissolved fraction, the available dilute-solution measurements are broadly consistent with the scaling theory of Dobrynin *et al.*^[288] In salt-free water, the overlap concentration follows approximately $c^* \propto N^{-2}$, consistent with strongly

extended chains. In excess salt, it approaches the good-solvent dependence expected when electrostatic interactions are screened. The radius of gyration decreases with added salt approximately as $R_g \propto c_s^{-1/5}$ over an intermediate concentration range. The reported values and salt dependence of the persistence length are not consistent across different studies. Further light scattering and intrinsic viscosity measurements on samples with well-characterised molar mass distributions and substitution patterns, analogous to the datasets available for sodium hyaluronate,^[289,298,310,311] are needed to establish the intrinsic and electrostatic contributions to the stiffness of CMC chains.

9.2. Rheological properties of CMC solutions and gels

The rheological behavior of CMC is governed by the relative contributions of electrostatic, associative and chain entanglement interactions. In dilute and semidilute unentangled solutions, electrostatic repulsion expands the chains and increases the viscosity. Added salt promotes electrostatic screening, decreasing the chain dimensions, viscosity and longest relaxation times. At higher polymer concentrations, electrostatic interactions become progressively screened, and the rheological behavior is controlled primarily by entanglements and associative interactions.^[12,320,395]

Highly substituted samples with $DS \geq 1$ display behavior characteristic of entangled polymer solutions: a Newtonian plateau at low shear rates, shear thinning at higher shear rates and liquid-like linear viscoelasticity. Weakly substituted samples with $DS \leq 1$ behave differently because unsubstituted cellulose patches generate associative interchain interactions. Their viscosity does not always approach a Newtonian plateau at low shear rates, and at sufficiently high concentrations they form weak physical gels. The gelation concentration depends on the average DS, the substitution pattern and the pH of the solution. The pH determines the effective charge of the chains: a higher effective charge increases interchain repulsion and weakens associative interactions. Additionally, for sufficiently high pH, cellulose becomes soluble in water, removing these interactions. Consequently, low- and high-DS CMCs display nearly identical behavior in concentrated NaOH solutions.

Thixotropic behavior is hypothesized to arise from the breakdown and re-formation of aggregates under shear and therefore has a different physical mechanism from weak gelation. Weak gelation does not require the formation of large multichain clusters, but only relatively long-lived interchain associations.

Our current understanding of how the substitution pattern influences CMC rheology remains largely qualitative. Although methods exist to quantify blockiness in CMC substitution, a correlation between blockiness and solution or gel rheology has not been established. Rheological measurements on samples with controlled blockiness and well-characterised molar mass distributions are needed to determine how substitution heterogeneity controls CMC gelation and thixotropic behavior.^[396–398]

9.3. Needed improvements in characterization and sample preparation

Purification by dialysis is standard practice for many commercial polyelectrolytes and is, in general, necessary to obtain reproducible results.^[399] The high purity of food-grade

CMC means that as-received samples often contain relatively low levels of residual salt, typically below one salt ion per 50 monomers, and can often be used without further purification. For technical and semi-purified grades, however, purity cannot be assumed. Dialysis against DI water followed by freeze-drying would help improve reproducibility of literature data.

Research on CMC would benefit from characterization of the degree of substitution and the molar mass. Many authors rely on manufacturer specifications for DS and M_w . DS values are usually accurate to within $\simeq 20\%$, but reported molar masses can deviate by factors of up to two, and batches sold under the same nominal molar mass do not necessarily exhibit consistent M_w . A survey of recent work shows that reliance on manufacturer data is the rule rather than the exception.^[70,235,400–410] As a result, many reported correlations between physical properties, for example solution viscosity, and molar mass^[334,411–413] are likely to be only qualitatively correct. Since the average DS can be measured by simple titration methods, authors should determine these values rather than rely on manufacturer specifications. Determination of the intrinsic viscosity in excess salt to obtain the molar mass is straightforward. Static light scattering can provide additional information, but, as discussed above, accurate values of $(dn/dC)_\mu$ need to be determined first.

The heterogeneity in degree of substitution and the specific substitution pattern play a central role in determining the rheological and associative behavior of CMC and its performance in formulated products. Despite this, studies that quantify DS polydispersity or substitution pattern remain rare.^[414] Systematic characterization of these features would allow for better interpretation of the flow behavior of CMC solutions and gels. Experimental techniques such as XRD are easy to perform and allow for at least some qualitative information on the substitution pattern of the polymers. More involved methods such as enzymatic depolymerization followed by residue analysis provide greater detail but require considerably more work. Similar considerations apply to the molar mass polydispersity, which, while important to understand flow properties, is not usually quantified in rheological studies.^[12,13,231,234–238,267,277] The development of methods to quantify molar mass distribution from rheological properties of salt-free polyelectrolytes should be helpful in this direction.^[415]

9.4. Outlook and open questions

The economic importance of NaCMC has resulted in considerable academic research into the physical properties of this polymer. However, given its complexity and inherent heterogeneity, many questions about its conformation and aggregation state in dilute solution remain unresolved. The collected data allow for a qualitative description of aggregation phenomena, and Burchard's fringed micelle model appears to correctly capture the existing experimental observations. Systematic light scattering studies on samples of various degrees of substitution in particular would be of interest to resolve some of the questions raised here. Arguably the largest gap in our understanding of CMC is the lack of quantitative relationships between substitution pattern and the properties of CMC solutions and gels. As discussed here, qualitative correlations can be established, for example, blocky substitution patterns promote aggregation and gel formation,

whereas more homogeneous substitution patterns generally do not. The main limitation is that studies of the physicochemical properties of CMC rarely report substitution pattern beyond the average DS, or, occasionally, the partial degree of substitution. Moving toward a predictive understanding of CMC solutions and gels will require studies that connect specific substitution patterns to specific material properties. Patent literature shows that different synthesis conditions lead to different performance targets, but the molecular basis for these differences remains poorly quantified.

Author contributions

CRedit: **Carlos G. Lopez**: Data curation, Formal analysis, Visualization, Writing – original draft, Writing – review & editing.

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374. Note that the dn/dc used is not measured at constant chemical potential.
375. Note that in some cases, such as polymerisation by monomer addition, the scaling exponent between $R_{g,z}$ and $M_w^{1/3}$, owing to the fact that the radius of gyration and molecular weight correspond to different moments of the distribution, cannot be related in a straightforward manner to the fractal dimension. Lacking any information on the polydispersity of these fringed micelles, we make the assumption that the polydispersity is constant.
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Appendix A. Refractive index of solutions

Appendix Table A1. Refractive index increment of NaCMC in various salt solutions.

Ref.	c_S [M]	$\frac{dn}{dc}$ [mL/g]	DS [-]	λ [nm]
[277]	no salt	0.17	0.8	–
[255] ^a	no salt	0.168	1.3	633
[278]	0.1 mM ^c	0.145	DS-independent (1–2.9)	–
[279]	0.05	0.137	0.66, 0.69	488
[280]	no salt	0.144	1.23	950
[281]	0.1	0.147	1	–
[282]	0.1	0.141	0.7	–
[279]	0.1	0.139	1.2	488
[283]	0.1*	0.156	DS-independent (0.8–2.9)	–
[268]	0.1	0.147	0.62–0.74	546.1
[230]	– ^b	0.163	DS-independent (0.75–1.25)	632.8
[284]	0.5	0.154	1.15	436
[285]	–	0.138	0.8	690

The added salt is NaCl except for Ref. ^[278] ^a TBACMC ^b presumably 0.02 or 0.1 M NaCl ^c added salt is NH_4NO_3 .

Appendix B. List of symbols

- a - exponent in MHS equation
- A - empirical parameter in Fuoss' viscosity equation
- A_2 - second virial coefficient
- a_{CI} - counterion surface area
- b - length of chemical monomer ($\simeq 5$ Å for CMC)
- B' - Empirical parameter in Fuoss' viscosity equation
- c - polymer concentration in units of moles of repeating units per volume
- C - polymer concentration in units of mass per volume
- $c_{\max}$ - polymer concentration at which the low-salt reduced viscosity peak occurs
- c_S - concentration of added salt in units of salt molecules per volume
- c^* - overlap concentration
- $\mathfrak{D}$ - dispersity or polydispersity
- dn/dC - refractive index increment in mass concentration units
- $(dn/dC)_\mu$ - refractive index increment measured at constant salt chemical potential
- d_F - fractal dimension
- e - elementary unit of charge
- f - fraction of monomers bearing a dissociated counterion
- G' - storage modulus
- G'' - loss modulus
- K - optical contrast factor (Eq. 7)
- K_η - prefactor in MHS equation
- k_B - Boltzmann's constant
- k_H - Huggins constant
- k_i - Reaction constants in the Spurlin model
- k_K - Kraemer's constant
- l_K - Kuhn length (intrinsic)
- $l_{p,0}$ —Intrinsic persistence length
- M_0 - Molar mass of a monomer
- M_n - number average molar mass
- M_w - weight average molar mass
- M_z - z-average molar mass
- M_{z+1} - $(z + 1)$ -average molar mass
- n - refractive index of solution

- n_0 - refractive index of solvent
- N - degree of polymerization in number of monomers
- N_A - Avogadro's constant
- N_K - number of Kuhn segments per chain
- $P(q)$ - Form factor of a chain
- q - scattering wave-vector
- R - end-to-end distance of a chain
- R_g - radius of gyration of a chain
- $R_{g,z}$ - z - averaged radius of gyration
- R_H - Hydrodynamic radius
- R_η - Viscosimetric radius
- S - Fractional area of solubility within the Hansen triangle
- t - reaction time
- T - Absolute Temperature
- $U_{\eta,f}$ - hydrodynamic ratio
- v_{CI} - counterion volume
- x_i - fraction of monomers with position i substituted ($i = 2, 3, 6$, see [Figure 1](#))
- x_m - mole fraction of non-solvent at the phase boundary
- x_C - Crystalline fraction
- χ_i - fraction of monomers which are unsubstituted ($i = 0$), mono-substituted ($i = 1$), di-substituted ($i = 2$) or tri-substituted ($i = 3$)
- δ_D - Hansen dispersion parameter
- δ_H - Hansen hydrogen-bonding parameter
- δ_P - Hansen polarity parameter
- ΔR - excess Rayleigh ratio
- ϵ_0 - vacuum permittivity
- ϵ_r - relative permittivity
- $\dot{\gamma}$ - shear rate
- κ^{-1} - Debye screening length
- λ - wavelength of scattering radiation
- η_{inh} - inherent viscosity
- η_{rel} - relative viscosity
- η_{red} - reduced viscosity
- η_{sp} - specific viscosity
- $[\eta]$ - Intrinsic Viscosity
- ω - angular frequency [rad/s]
- ρ —Dimensionless ratio ($\equiv R_g/R_H$)
- σ - standard deviation of the DS distribution
- ν - frequency [Hz]
- θ - scattering angle
- μ - mean of DS distribution

Appendix C. List of abbreviations

- ASTM - American Society for Testing and Materials
- AGU - anhydroglucose unit
- AFM - atomic force microscopy
- Cell - Cellulose
- CMC - carboxymethyl cellulose
- DS - degree of substitution
- HBR - historical Tylose grade name
- IPA - Isopropanol
- GPC - Gel permeation chromatography
- LS - light scattering

- MHS - Mark-Houwink-Sakurada
- DI - deionized
- SANS - small angle neutron scattering
- SAXS - small angle x-ray scattering
- SLS - static light scattering
- DLS - dynamic light scattering
- TMA - tetramethyl ammonium
- TBA - tetrabutyl ammonium
- XRD - x-ray diffraction