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New hydrophobically modified carboxymethylcellulose derivatives

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New hydrophobically substituted carboxymethylcellulose derivatives with different percentages of modification by hexadecylamine (from 0.9 to 6% per monomeric unit acid group) were obtained by amidation of the carboxyl group by different methods. The percentage of modification (% HDA) was controlled by conductimetric titration and quantitative ^{13}C NMR spectra on cellulase hydrolyzed oligomers. The least degradation (checked by GPC measurements), was found on coupling the hexadecylamine with the acid form of CMC activated by *N,N'*-dicyclohexylcarbodiimide (DCCI) in dry dimethylsulfoxide. In the dilute range, the viscosities decreased due to the contraction of the hydrophobically modified CMC derivatives by intramolecular interactions. These effects are counterbalanced by increasing the ionic strength. Rheological measurements indicate an enhancement of the apparent viscosity for %HDA ~6, suggesting the establishment of intermolecular interactions, disrupted as the shear rate increases, in the semidilute range, beyond the overlap concentration ($C_p^* \sim 1.5\,\mathrm{g\,liter^{-1}}$). This behavior is confirmed by a moderate shear thinning effect in contrast with the precursor for which the viscosities show no shear dependence up to $C_p^* \sim 5.3\,\mathrm{g\,liter^{-1}}$ (Newtonian behavior). © 1997 Elsevier Science Ltd

INTRODUCTION

Hydrophobically modified (or associating) (synthetic or natural) water-soluble polymers (HMWSP) (Glass, 1989) have captured the attention of macromolecular chemists for about ten years. Historically, the first polysoap, now called "associative polymer", was prepared by the partial quaternization of poly(2-vinylpyridine) with *n*-dodecyl bromide (Strauss and Jackson, 1951). Viscosity measurements indicated abnormally compact molecular dimensions in aqueous solution, suggesting intramolecular interactions. Typically, these materials are water-soluble ionic or neutral polymers containing a small amount of hydrophobic aliphatic or perfluoro chains or aromatic groups (up to 5 and even 10%, for the ionic polymer). They form hydrophobic microdomains, which possess similar properties to those of surfactant micelles, solubilizing water-insoluble organic compounds like the pyrene or biopolymers such as some hydrophobic proteins.

The preparation of such materials has been carried out by copolymerization of the appropriate comonomers (McCormick *et al.*, 1989; Hill *et al.*, 1993) or modification of a preformed synthetic (Wang *et al.*, 1991; Magny *et al.*, 1994) or natural precursor. The last synthetic route has been applied to cellulose derivatives. Many studies have been devoted to the hydrophobically modified polysaccharides. The special interest in such low cost industrial materials is explained by their interesting properties, which provide uses as surface active agents, associative thickeners in oil recovery, latex paint or as support for enzyme immobilization. In eighty years, Landoll (1989) was the first investigator to report the grafting of a small amount of hydrophobic long-chain alkyl residues via the 1,2-epoxyalkane on the (hydroxyethyl)cellulose, and the exceptional solution thickening properties of these modified semisynthetic polysaccharides. We can also mention the more recent synthesis and properties in solution of palmitoyl and cholesteryl modified pullulan derivatives (Akiyoshi *et al.*, 1993) and the rheological properties of some other derivatives of

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pullulan obtained by esterification with aromatic substituents, which suggest more compact conformation than that of pullulan itself (Mocanu *et al.*, 1995).

Nonspecific chemical modifications or various grafting processes of vinyl monomers on the carboxyl-containing polysaccharides have been the subject of a great number of early papers or patents (Kricheldorf, 1992; Yalpani, 1988). These polysaccharides are known to be easily degraded chemically with alteration in monomer structure as well as a reduction in molecular weight.

Carboxymethylcellulose (CMC) is a very low cost industrial semisynthetic charged polysaccharide, synthesized for the first time by Jansen (1918). The cross-linked CMC is largely used as a weak acid cation exchanger. As it is biodegradable in a few weeks, at room temperature, its applications include uses in cosmetics, as a food thickener and in the encapsulation of drugs. At high temperature (10 min at 120°C), the viscosity continuously decreases, due to chain scission (Rao *et al.*, 1981).

In the present paper, our two main objectives were:

(1) To determine the least degradative method for substituting the carboxymethylcellulose with a long hydrophobic amino chain.
(2) A preliminary study of the rheological behavior, in solution, of these modified carboxymethylcellulose derivatives, in order to understand the nature of the hydrophobic interactions in these solutions.

MATERIALS AND METHODS

Materials

CMC ($M_w \sim 300\,000$) with a degree of substitution DS$\sim$0.9 (carboxymethyl group per anhydroglucose unit), was supplied by Aqualon Ltd (France). It was twice precipitated from aqueous solution in a large excess of ethyl alcohol, then dialyzed against Milli-Q (Millipore) water, evaporated as a film and dried at ~60°C under vacuum (3–5 mm Hg). The hexadecylamine (HDA) and the *N,N'*-dicyclohexylcarbodiimide (DCCI) were commercial products from Fluka. Dimethylsulfoxide (DMSO) was distilled on CaH_2. *Trichoderma reesei* cellulase is a Sigma product.

The modified CMC derivatives were obtained using the following method: the acid form of CMC was dialyzed against HCl 0.1 N, then against water until neutral. The solution polymer was concentrated and dried as a film in a high velocity air stream without heating (or better as a powder after atomization) and finally under vacuum. 2 g of this film (8.47 mM) were dissolved in 100 ml of DMSO for 2 days. Then one equivalent of DCCI was added under stirring in a dry atmosphere. After 30 min, one equivalent of HDA in $CHCl_3$ solution was mixed with 5 mg of dimethylaminopyridine as catalyst. The reaction time was 1 day at room temperature. Different extents of modification were obtained by changing the ratio of CMC/HDA. After neutralization, the modified CMC was purified in the same way as the source material.

Nomenclature

The reactions used to modify the CMC and some properties of the derivatives and the precursor are listed in Table 1. The designation of the samples is as follows: **CMC** is the precursor, **CMC-A** is the modified polymer obtained by method A described above. The sample called CMC-A-6% contains 6% of hexadecylamine randomly distributed per monomeric unit acid group. **CMC-B** was obtained using the acid chloride in large excess following the addition of HDA as reported by Rogovin *et al.* (1961). **CMC-C** was synthesized following Van der Horst *et al.* (1994), using as basic catalyst an excess of hexadecylamine or the *N*-phenyl, *N*-naphthylamine. **CMC-D** was prepared by adapting the method of Vogt *et al.* (1995), the acid form of CMC was not isolated.

Methods

The degrees of substitution of the carboxylic group COOH (DS_{COOH})

For both CMC and modified CMC, these were established by conductimetric back titration, under argon at 25°C, following the method of Eyler *et al.* (1947). The percentage of modification by hexadecylamine per monomeric unit (% HDA) is given by their differences. A typical measurement was made in duplicate as follows: to 200 mg of sample dissolved in 50 ml of water was added 1 ml of N NaOH; the solution was then titrated with 0.1 N HCl. The % HDA found are in satisfactory agreement with the nitrogen microanalysis. The contents of modified CMC are presented in Table 1. As the moisture percentages can reach 14%, the concentrations were determined on a dry weight basis (see below).

Preparation of the solutions

For measurements at low concentrations, the polysaccharides were dissolved in Milli-Q water over 12 h at 4°C. The solutions were clarified through an 8 μm Millipore filter. To determine the exact concentrations, 10 ml of the solution (about 10–30 mg) were evaporated in an oven at 80°C during one night. The sample, cooled in a dessicator, was weighed before and after evaporation. For all sample solutions, whatever the concentration, NaCl was added to obtain the desired ionic strength *I*. In the semidilute range, the polymer solutions were prepared by adding the appropriate amount of solid polymer directly to 0.1 M NaCl solution.

Table 1. Synthesis conditions and characteristics of modified CMC derivatives

Samples	Methods used	% HDA[a]	[η] (ml g^{-1})	k'
CMC	Precursor	0	620	0.5
CMC-A-0.9%	DMSO/DCCI(1eq.)/ HDA(1eq.)	0.9	380	0.6
CMC-A-2.4%	DMSO/DCCI(1 eq.)/ HDA(1eq.)	2	360	0.7
CMC-A-4.6%	DMSO/DCCI(1eq.)/ HDA(1eq.)	2.4	411	0.5
CMC-A-5.3%	DMSO/DCCI(1eq.)/ HDA(1eq.)	3.7	370	0.7
CMC-A-6%	DMSO/DCCI(1eq.)/ HDA(1eq.)	6.0	480	1.2
CMC-B[b]	$SOCl_2$ + HDA (DMF) 30% excess[b]	1.0	460	0.5
CMC-C[c]	40% excess of HDA[c]	9.0	230	1.4
CMC-D[d]	CMCNa + $p\phi SO_3H$ DMSO/DCCI(1eq.)/ HDA(1eq.)[d]	4.5	410	0.7

[a] % of modification from conductimetry titration.
[b] Following Rogovin *et al.* (1961).
[c] Following Van der Horst *et al.* (1994).
[d] Adapted from Vogt *et al.* (1995).

Rheological measurements

These were performed (i) in dilute solutions with a low-shear 30 Contraves viscosimeter, (ii) in semidilute solutions using a Carrimed CSL 100 controlled-stress rheometer (Carri-Med Ltd, Dorking, UK).

Size exclusion chromatography

Two different sets of coupled columns packed with TSK gel were used: (i) G4000PW/G6000PW columns (Toyo Soda) using a 0.1 M $LiNO_3$ solution as eluent (system A); (ii) SW_{XL} 3000/4000 columns (Tosohass), using a 0.05 M phosphate buffer at pH ~6.8 as eluent (system B). In the two sets of experiments, the columns were coupled with an on-line multiangle laser light scattering detector (Dawn DSP-F, Wyatt Technology, USA) and a refractive index detector (Shimadzu). The solutions were clarified through a 0.45 μm Millipore filter. All samples were injected through a 400 μl loop (system A) and a 100 μl loop (system B), at a known concentration of ~2–3 g liter^{-1}. The details of the technology and associated Astra software were described elsewhere (Picton *et al.*, 1995). d*n*/d*c* was measured with a Brice Phoenix differential refractometer. A value of 0.166 ml g^{-1} was used for CMC and 0.143 ml g^{-1} for the modified samples.

NMR spectra

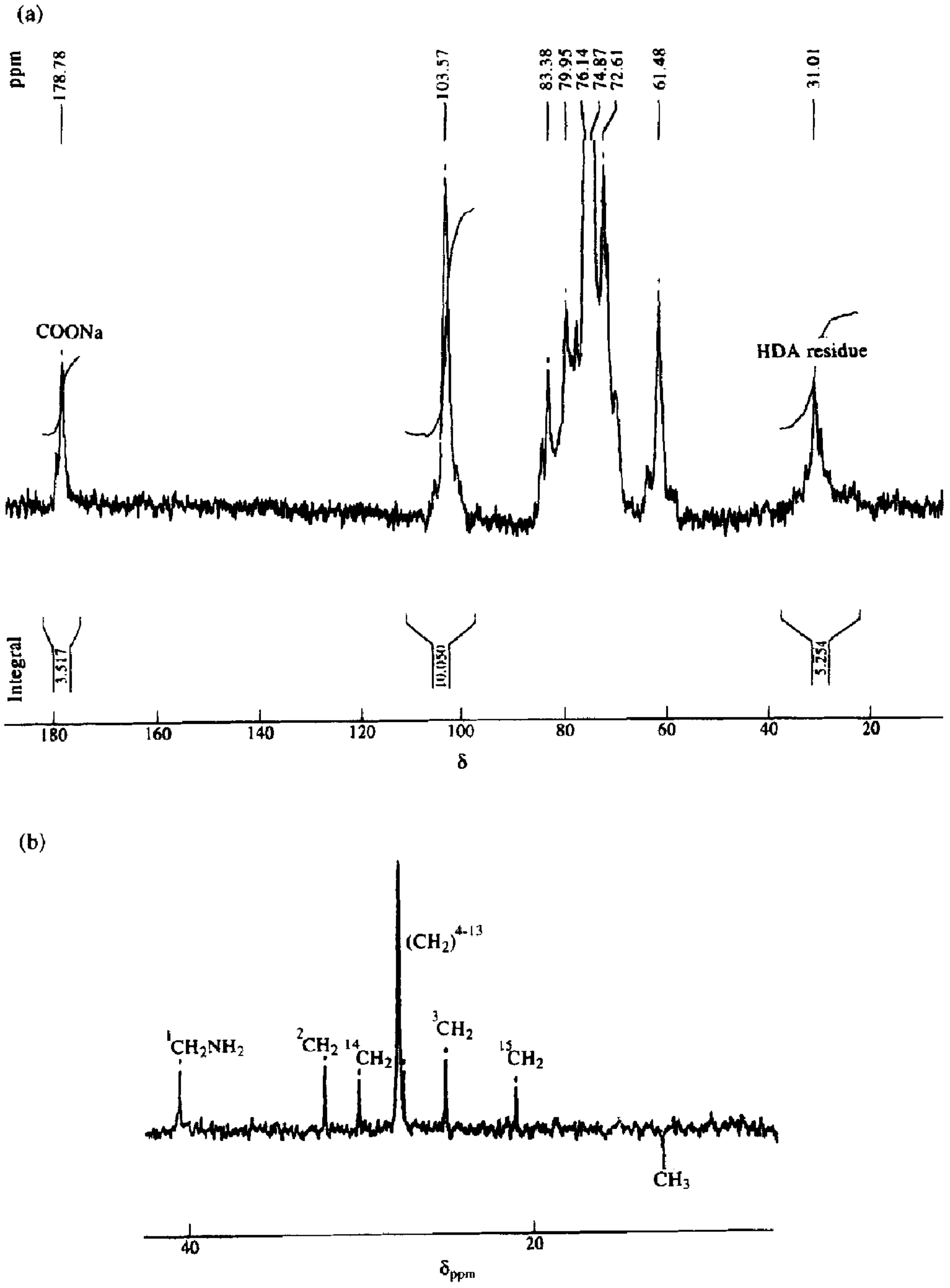
NMR spectra were recorded on a Brucker ARX 400 spectrometer, equipped with a multinuclear 10 mm probe. The ^{13}C frequency was 100.62 MHz. An aqueous solution of 2,2,3,3,-tetramethylsilylpropionate (TMPS) was used as chemical shift reference. Taken as examples, CMC-A-6% and its oligomer were compared at the same concentration (20% by weight) and the same pH (~7.7) in D_2O. Figure 1(a) shows the spectrum of the modified polymer at 340 K. The spectrum was broadband decoupled and obtained with nuclear Overhauser enhancement. Figure 1(c) displays the spectrum of CMC-A-6% hydrolyzed over one night by cellulase at 50°C and pH ~5. The spectrum was recorded at 315 K to avoid undesirable secondary reactions. The spectrum of free HDA is given in Fig. 1(b). For the hydrolyzed sample, quantitative information required a gate inverse pulse sequence with broadband decoupling; the fit angle was 90° (14.5 s) and the relaxation delay was 10 s. In addition, a *J*-modulated spin echo experiment which allows the determination of the multiplicity of the carbon atoms was performed at 315 K.

RESULTS AND DISCUSSION

Choice of the reaction to modify hydrophobically CMC

Our attention was focused on some classical organic reactions, to modify the carboxylic acid functions of the CMC into amide group. In view of the conflicting nature of the modification of hydrophilic polysaccharides with hydrophobic reagents, and to compare the physical properties of the modified polymers obtained, some features have to be confirmed, mainly the degree of modification (DS), the possible chemical degradation of the main chain or undesirable secondary reactions.

In a previous report, amidation of the carboxylic groups of CMC was achieved at pH ~5, in an heterogeneous medium, water and hexadecylamine, in the presence of the water-soluble *N*-


(a)
ppm
178.78
103.57
83.38
79.95
76.14
74.87
72.61
61.48
31.01
COONa
HDA residue
Integral
3.517
10.050
5.254
180
160
140
120
100
80
60
40
20
δ
(b)
(CH2)4-13
1CH2NH2
2CH2
14CH2
3CH2
15CH2
CH3
40
20
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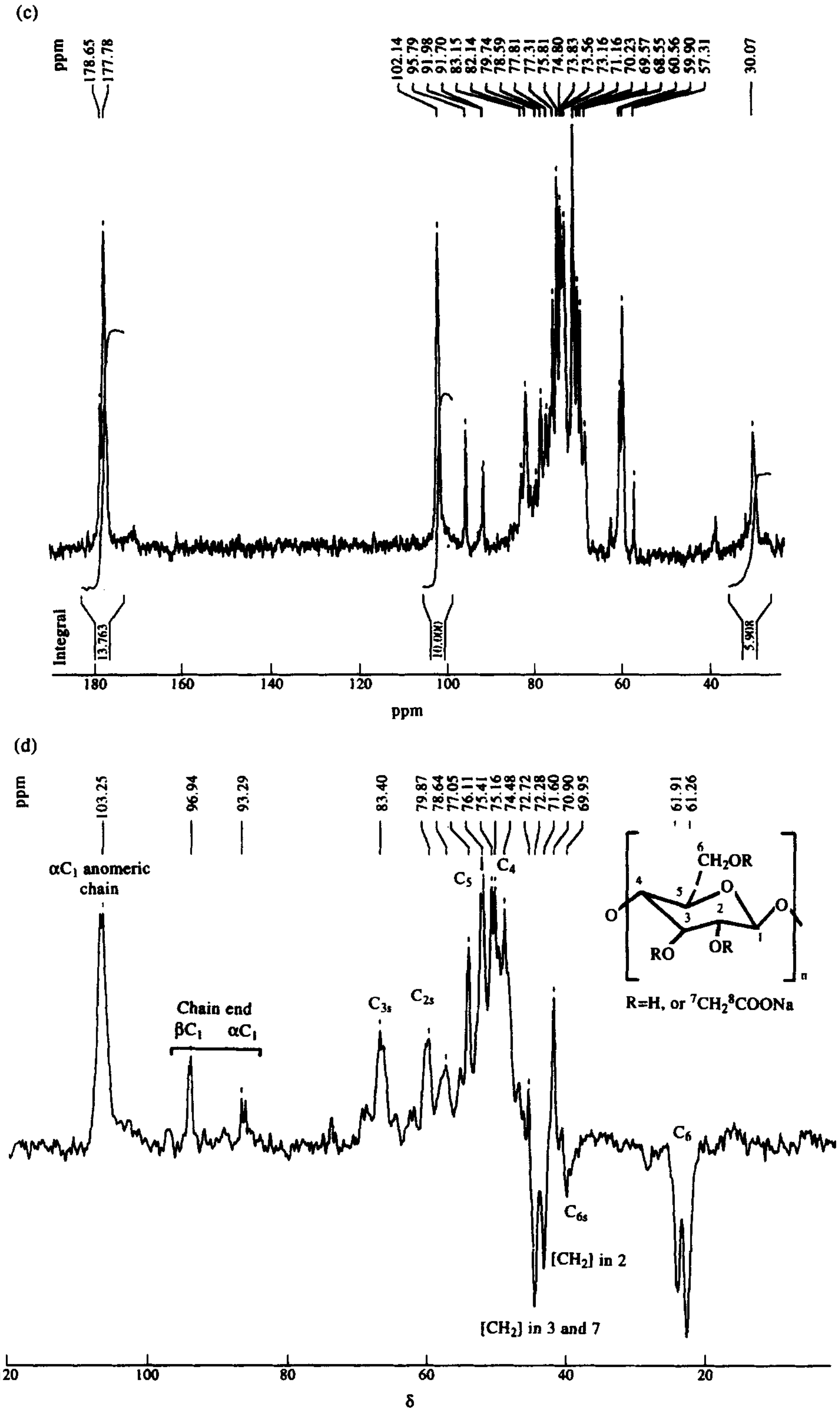

Fig. 1. ^{13}C-NMR spectra of CMC-A-6 and its oligomer in D_2O: (a) CMC-A-6% (~60 000 scans, at 323 K) (%HDA ~6); (b) HDA in $CDCl_3$, (c) CMC-A-6% hydrolyzed by cellulase (~3600 scans at 323 K); (d) *J*-modulated spin echo spectra of cellulase hydrolyzed CMC-A-6%.

(dimethylaminopropyl)-N'-ethyl carbodiimide (EDC). This method has been used for the synthesis of the alginic acid and xanthan gum amides (Yalpani, 1988) and also with proteins. A comparison of the solution properties of the modified CMC and its parent precursor was disappointing because of molecular weight degradation and a very low extent of modification occurred as a result of the coupling reaction (Picton *et al.*, 1996). In fact, carbodiimide treatment is known to produce interresidue lactonization at low pH, and intense depolymerization during the EDC activation of glycoaminoglycanes was observed (Inoue and Nagasawa, 1982) with racemization in some cases. The mechanism of the depolymerization is not yet completely understood.

Common methods used to prepare polysaccharide amides by direct condensation of their carboxyl group with amines are scarce. We can mention:

(1) Amidation of the free acid form in homogeneous or heterogeneous medium, by dehydration of the long chain ammonium salts of CMC, through azeotropic distillation in xylene at 140°C (Van der Horst *et al.*, 1994);

(2) Amidation of the acid form of CMC obtained *in situ* in a defined amount, adapted from Vogt *et al.* (1995).

The results obtained with the four different types of reactions are given in Table 1. Only reactions A or D are almost quantitative. Methods B and C use a large excess of reagents and C degrades the polysaccharide extensively (Table 1). The rheological measurements were made on the samples obtained with method A and especially on CMC-A-6%, which shows the lowest degree of degradation.

Sodium carboxymethylcellulose is a copolymer of two units: β-D-glucose and β-D-glucopyranose 2-*O*-(carboxymethyl)-monosodium salt, not randomly distributed along the macromolecule, which are linked via β-1,4-glycosidic bonds. The substitution of the hydroxyl groups by the carboxylmethyl group is slightly preponderant at C-2 of the glucose (Reuben and Conner, 1983). It is a weak acid with $pK_a \sim 3.8$. CMC is easily degraded by cellulase. This methodology has been used previously to determine the DS_{COOH} by ^{13}C NMR spectra of high molecular weight CMC (Gautier and Lecourtier, 1991).

In Fig. 1(a), the ^{13}C NMR spectrum of CMC-A-6% (pH ~7.7) is shown. A single signal of the anomeric C-1 appears at 102 ppm and the characteristic peak of the carboxylate group COONa group is present at 178.9 ppm, whereas the signal due to the CONH amide group is not intense enough to be detected. The modification of the polymer by HDA is confirmed by a specific signal at ~31 ppm. Indeed, this peak was assigned from the ^{13}C spectrum of the free HDA dissolved in $CDCl_3$ (Fig. 1(b)) (HDA is not soluble in D_2O), which displays a major broad signal at 29 ppm attributed to the 10 carbons at C4-13 of the amine chain, and 6 minor peaks between 12 and 42 ppm assigned to the remaining carbon atoms. In Fig. 1(c), the spectrum of the same polymer but hydrolyzed by cellulase is given. The peak at 31 ppm was integrated and its area, related to that of the anomeric C-1 signal at 102 ppm, used to determine the percentage of modification. It gives a % HDA of 5.9 in agreement with that found by conductimetric titration results. For the native polymer, the data from ^{13}C spectrum, although not quantitative, give a similar value of % HDA ~5.3, which closely matches the above value.

As expected, the resolution of the hydrolyzed sample (Fig. 1(c)) is much better than that of the polymer. The number of resolved singlets is higher, and two new signals appear at 92 and 96 ppm, which are assigned to the anomeric carbons at the end of the oligomeric chains; they correspond to anhydroglucose units in either α or β configuration. The presence of these signals clearly indicates that the enzymatic degradation is efficient for the modified CMC-A-6% and their relative intensities give the relative proportions of the α anomer (43%) and the β anomer (57%). The C-2 and C-3 atoms substituted by the carboxymethyl groups give two distinct signals respectively at 83.4 and 79.9 ppm. From the *J*-modulated spin echo (Fig. 1(d)), the hydroxymethyl groups at C-2, C-3 + C-7 and C-6 are easily identified at 71.6, 72.3 and 69.9 ppm.

Rheological properties

Viscosity properties of samples obtained by methods B, C and D

The reduced viscosity (η_{red}) of dilute solutions of polymers changes with the concentration, according to the Huggins relationship:

$$\eta_{red} = \eta_{sp}/c = [\eta] + k'[\eta]^2 c$$

where k' is the Huggins constant, depending on the nature of the polymer–polymer interactions in solution. For a random coil polymer, a common value of 0.3–0.8 is found for k' and larger values indicate associations.

The intrinsic viscosities and the Huggins constant k' were determined for CMC-B, CMC-C, CMC-D and for the precursor. The plots of reduced viscosity, in 0.1 M NaCl, are given in Fig. 2 as a function of the polymer concentration. The critical concentration of the precursor ($C^* = 5.3\,\mathrm{g\,liter^{-1}}$) is related to significant coil overlap, which is the upper limit of the dilute regime. For each modified polymer solution in the dilute regime, the intrinsic viscosities are distinctly lower than for the precursor and the Huggins constant k' remains very small, suggesting intramolecular interactions and/or molecular weight degradation. For this regime, at equivalent M_w, the modified derivatives should adopt a more compact conformation than the carboxymethylcellulose if intramolecular interactions

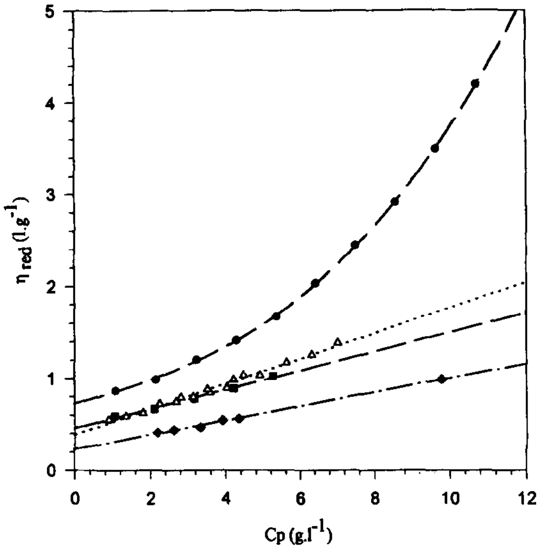

Fig. 2. Reduced viscosities as a function of the polymer concentration, in 0.1 M NaCl. CMC (●), CMC-B (■), CMC-C (◆), CMC-D (△)

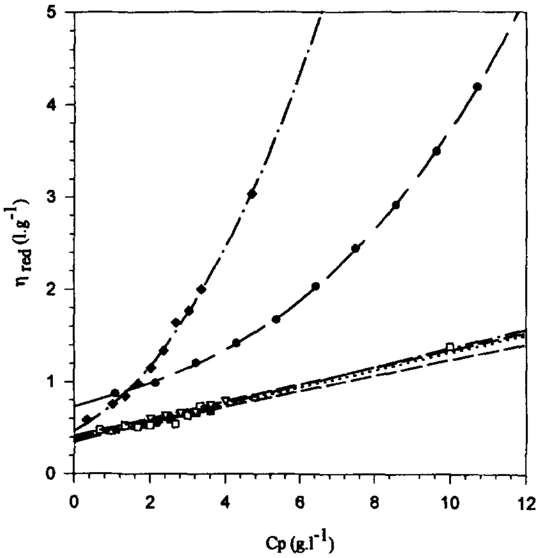

Fig. 3. Reduced viscosities as a function of the polymer concentration in 0.1 M NaCl, for CMC and CMC-A (DMSO/DDCl). CMC (●), CMC-A-0.9% (■), CMC-A-2.4% (△), CMC-A-4.6% (▽), CMC-A-5.3% (□), CMC-A-6% (◆).

occur. In the range of higher concentrations ($C_p > C^*$) the viscosities remain lower for the modified polymers than for the precursor, suggesting that these modified polymers cannot establish associative interactions.

A typical set of flow curves ($\log \eta_{app}$ plotted against $\log \dot{\gamma}$, $\dot{\gamma}$ being the shear rate) have been obtained for CMC and CMC-D at $C \sim 3$ g liter^{-1} (data not shown). For the low shear range (from 0.017 to 128.5 s^{-1}), the precursor and CMC-D show Newtonian behavior, and the flow curve of the modified polymer CMC-D is always below the CMC curve.

Viscosity properties of samples obtained by method A

The decrease of intrinsic viscosities of modified polymers could be ascribed to a coil contraction or a molecular weight degradation of the precursor, or a combination of both. In order to clarify these two points, the influence of polymer concentration was investigated for CMC-A.

Influence of the polymer concentration

The viscosity variation as a function of the polymer concentration is presented in Fig. 3. At a level of incorporation smaller than 6%, the intrinsic viscosities are lower than for the precursor, and the Huggins constants are not modified, suggesting low polymer–polymer interactions (Table 1). This behavior can be explained by intramolecular associations and consequently a contraction of the hydrodynamic volume or a possible degradation. The amount of hydrophobic aliphatic chains between 0.9 and 5.3% is much too low to induce an associative character, and probably only intramolecular interactions are present.

In contrast, for the CMC-A-6% in dilute solution, the intrinsic viscosity is also lower than for the unmodified precursor, but the Huggins constant is 2.4 times higher ($k' = 1.2$ instead of 0.5 for the CMC). These results suggest the existence of intermolecular and/or intramolecular interactions.

In the semidilute range, CMC-A-6% shows a large increase in viscosity in comparison with CMC, and the critical concentration of the modified polymer is much smaller ($C^* = 1.5$ g liter^{-1}) than that of the precursor ($C^* = 5.3$ g liter^{-1}). This behavior agrees with the results reported for different kinds of HMWSP and can be related to the occurrence of intermolecular associations responsible for the chain overlap. Therefore, in order to know whether intramolecular associations are also present, the influence of ionic strength was investigated.

Influence of the ionic strength in dilute solution

First, at the fixed concentration $C_p \sim 1$ g liter^{-1}, the dependence of the reduced viscosity versus the ionic strength was plotted for CMC and CMC-A-6%. Both curves reveal a continuous decrease in viscosity upon addition of NaCl from 0.01 to 2 M (Fig. 4). At low ionic strength (0.01 M), they display the same reduced viscosity. The electrostatic repulsions prevail over the associative interactions and consequently the coil expansion is maximum, evidenced by large values of viscosities (polyelectrolyte effect). At high ionic strength (≥ 1 M), the modified polymer has clearly a lower reduced viscosity (η_{red}) than its parent polymer. The electrostatic repulsions between the polymer charges are screened, inducing a contraction of the polyelectrolyte chain into a more compact coil than CMC attributed to aggregation through the alkyl chains; consequently, intramolecular hydrophobic interactions are possible.

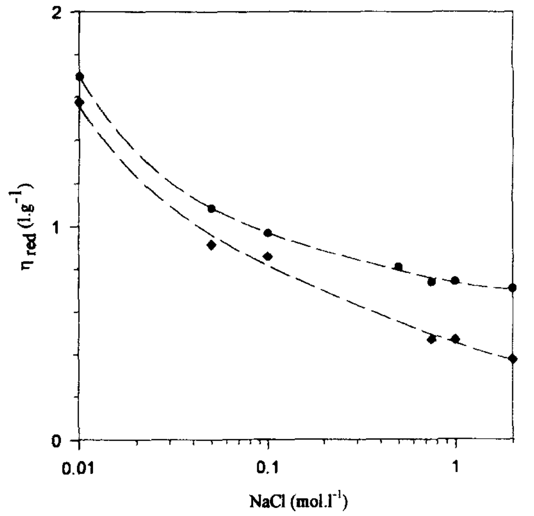

Fig. 4. Reduced viscosities as a function of NaCl concentration in dilute solution ($C_p \sim 1$ g liter^{-1}). CMC (•), CMC-A-6% (◆).

The ratio $\eta_{red1M}/\eta_{red0.01M}$ for CMC and CMC-A-5.3% have the same value (44%) whereas for CMC-A-6% it is lower (30%). Thus, the aggregation mechanism due to hydrophobic interactions is negligible for modified polymers with % HDA < 6.

For a fixed value of ionic strength I, the variation of the reduced viscosity of CMC-A-6% versus the polymer concentration was plotted. Figure 5 shows two plots respectively for $I = 0.1$ M NaCl and $I = 1$ M. The value of the intrinsic viscosity, lower in 1 M than in 0.1 M, confirms the results of Fig. 4. As expected, the addition of NaCl to an associative polyelectrolyte solutions leads to a more pronounced decrease in viscosity than for a hydrophilic polyelectrolyte possessing the same charge density.

For relatively low polymer concentration ($C_p \sim 1$ g liter^{-1}), this strongly decreasing viscosity indicates the occurrence of intrachain associations due to hydrophobic interactions (Wang *et al.*, 1991).

In dilute solution ($C_p \leq C^*$), Fig. 5 shows that in 0.1 M NaCl the Huggins constant is slightly higher ($k' = 1.2$) than in 1 M NaCl ($k' = 0.8$) and the viscosity significantly increases above the limit of the dilute regime ($C \geq C^*$); both features are indicative of intermolecular associations. Conversely, in 1 M NaCl, the viscosity does not show the same behavior and it can be suggested that intramolecular associations are favoured even for $C_p > C^*$.

These trends confirm that for ionic associative polymers, the coil expansion in solution is governed by the balance between two forces acting in opposition: the electrostatic repulsions between the fixed charges of the polymer chain and the attractive hydrophobic interactions between the alkyl groups. Intramolecular and/or intermolecular hydrophobic associations are favoured by increasing the salinity.

Influence of the shear rate in dilute and semidilute domains

CMC and modified CMC derivatives were dissolved at a concentration of 3 g liter^{-1}. This value belongs to the dilute range for CMC and CMC-A-5.3% and to the semidilute range for CMC-A-6%. For these three solutions, the shear dependences of the viscosity are given in Fig. 6.

At low shear rates (from 0.017 to 128.5 s^{-1}), the flow curves obtained for CMC and CMC-A-5.3% have a Newtonian profile (for CMC-A-5.3%; because the sensitivity limit of the viscometer is approached, the measurements are not reliable in the range 0.017 to 0.945 s^{-1}). For CMC-A-5.3%, the viscosity is smaller

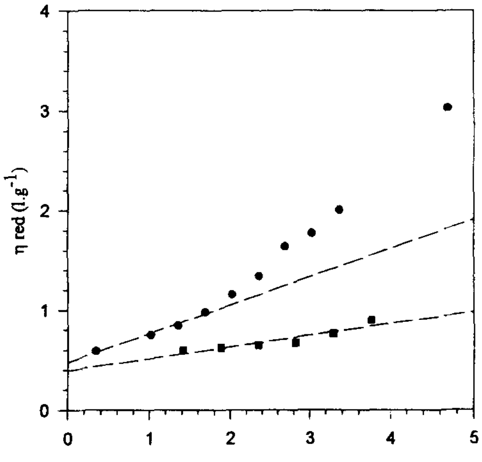

Fig. 5. Reduced viscosities versus the concentration of polymer for CMC-A-6%, at different ionic strengths: 0.1 M NaCl (•), 1 M NaCl (■).

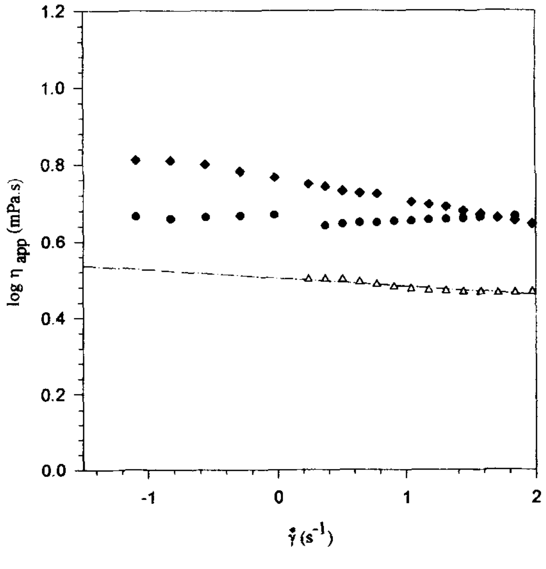

Fig. 6. Influence of the shear rate on the apparent viscosities of CMC and CMC-A ($C_p \sim 3$ g liter^{-1}). CMC (•), CMC-A-5.3% (△), CMC-A-6% (◆).

than for the precursor, due to the predominance of intramolecular associations, but for CMC-A-6% it is higher. In fact, at the operating concentration $C_p = 3\,\mathrm{g\,liter^{-1}}$, the critical overlap concentration ($C^* \sim 1.5\,\mathrm{g\,liter^{-1}}$) is exceeded and intermolecular associations between modified chains appear which are responsible for the enhancement of viscosity (Landoll, 1989).

The rheogical behavior was also investigated at $C_p = 8\,\mathrm{g\,liter^{-1}}$ and in 0.1 M NaCl for both CMC and CMC-A-6% ($C_p = 8\,\mathrm{g\,liter^{-1}}$ belongs to the semidilute range for both polymers), in a large range of shear rate (from 1 to $2000\,\mathrm{s^{-1}}$). The corresponding curves are shown in Fig. 7. As none of these curves exhibits an hysteris loop, it can be concluded that both CMC and CMC-A-6% give pseudoplastic rather than thixotropic solution.

The precursor sample initially displays Newtonian behavior until $\sim 100\,\mathrm{s^{-1}}$, and then for shear values higher than this value, typical shear thinning behavior appears. In contrast, the apparent viscosity of CMC-A-6% always decreases. At low shear rates, high values of the low shear viscosity are observed, which are due to the establishment of intermolecular hydrophobic associations in a concentration range higher than the critical C^*. At the highest shear rates (above $60\,\mathrm{s^{-1}}$), the values of the apparent viscosities are slightly smaller than for CMC because these intermolecular associations are broken. This decrease in the apparent viscosity indicates a reduction in the hydrodynamic volume. The modified carboxymethylcellulose exhibits a more compact conformation than the parent CMC because of the contribution of intramolecular associations, probably unaffected by the shear. But, a slight degradation could not be excluded.

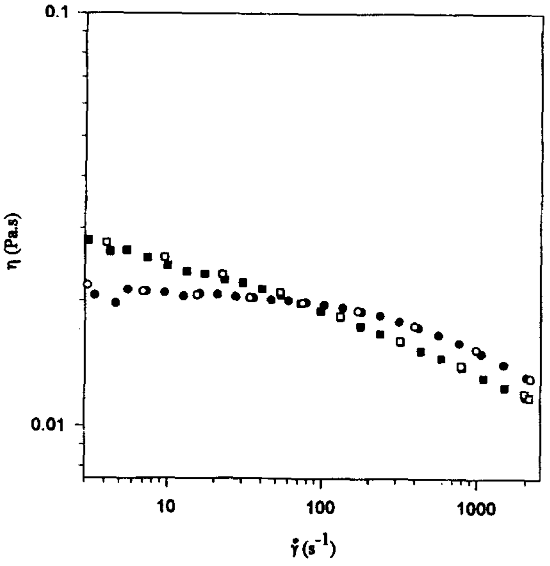

Fig. 7. Rheological behavior in the semidilute range ($C_p \sim 8\,\mathrm{g\,liter^{-1}}$) in 0.1 M NaCl. CMC (shear rate increasing ●), CMC (shear rate decreasing ○), CMC-A-6% (shear rate increasing ■), CMC-A-6% (shear rate decreasing □).

Size exclusion chromatography coupled to multi-angle laser detector

The physical–chemical characteristics of CMC and modified CMC derivatives have been examined firstly with the TSK G4000PW/G6000PW columns, in 0.1 M $LiNO_3$ as eluent (system A) and secondly with the TSK 3000/4000 SWXL (system B) in 0.05 M phosphate solution (in which the modified CMC derivatives are moderately soluble).

Figure 8(a) and (b) display the results obtained on CMC and on CMC-A-4.6%, using system A. The precursor presents a low angular dependency of the scattered light (Fig. 8(a)).

In contrast, an important angular dependency is observed for the modified CMC, abnormally eluted at a large elution volume in the salt peak (Fig. 8(b)). These results suggest the presence of a heterogeneous population of polymers and aggregates, which are retained on filters and/or these columns (until 40%), so the determination of the molecular weight of modified CMC is very difficult or even impossible.

For minimizing the retention on the columns, the polymers were investigated with system B, normally used for proteins, and previously used for modified hydrophobically pullulans (Akiyoshi *et al.*, 1993), and at sufficient ionic strength to avoid electrostatic effects (Roure *et al.*, 1996).

The curves shown in Fig. 9(a) to (c) illustrate the

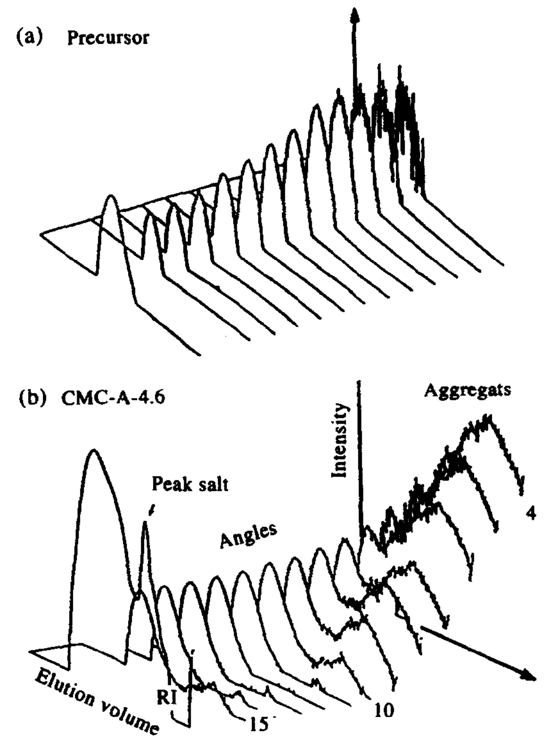

Fig. 8. Scattering envelope for the precursor CMC (a) and modified CMC-A-4.6% (b), in 0.1 M $LiNO_3$ between 21.7° (detector 4) and 135° (detector 15) (SEC/MALLS coupling on line, using the A columns).

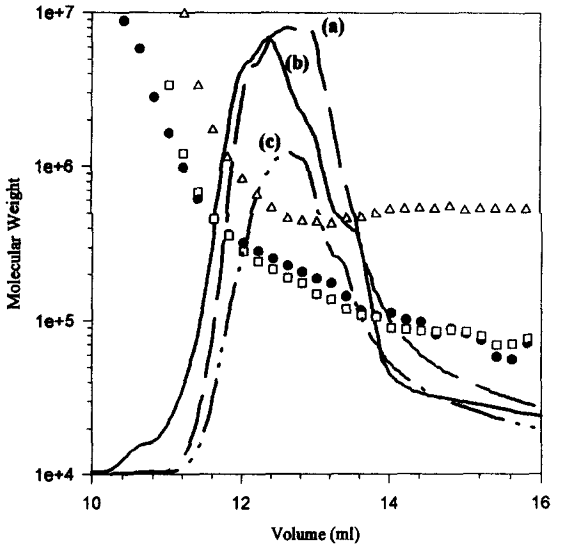

Fig. 9. Compared elution profile (detected by refractive index) of the precursor (a), modified CMC-A-5.3% (b), and CMC-A-6% (c), in a 0.05 M buffer, using the B colomns with the distribution of molecular weights of the same samples (calculated by the multi-angle Wyatt detector). CMC (•), CMC-A-5.3% (□), CMC-A-6% (△).

dependence of the molecular weight on the elution volume for CMC, CMC-A-5.3% and CMC-A-6%. CMC and CMC-A-5.3% have nearly the same molecular weight distribution directly determined by the scattered light detector. Conversely, for the CMC-A-6%, large molecular weights are observed and elution is slightly delayed. It can be assigned to the presence of aggregates of high molecular weight (induced by the intermolecular interactions) but, however, of smaller hydrodynamic volume when compared to the precursor.

CONCLUSION

This paper reports some interesting results on new hydrophobically modified carboxymethylcellulose derivatives prepared under different conditions.

The modification by a long-chain amine, in organic medium (DMSO) via the acid form of CMC and after activation of the carboxylic groups with the *N,N'*-dicyclohexylcarbodiimide (DCCI), seems to cause least degradation. The very important feature of this method is that the acid form of CMC can be made completely soluble in water and can be swollen by an organic medium. The procedure used will be detailed in a future paper.

The results also indicate that the incorporation of hydrophobic substituents (in the range 0.9–5.3%) induces intramolecular associations in dilute solutions. For a modification of 6%, the establishment of intermolecular interactions is observed in the semidilute range of concentrations, as illustrated by a shear thinning effect, in contrast with the Newtonian behavior of the precursor. Besides, this modified carboxymethylcellulose (CMC-A-6%) shows some peculiar associative properties.

This work will be extended to study the effect of other parameters on the rheological properties of the CMC-A samples. It will serve to complement the results obtained by SEC/MALLS. The details will be given elsewhere.

REFERENCES

Akiyoshi, K., Deguchi, S., Moriguchi, N., Yamaguchi, S. and Sunamoto, J. (1993) *Macromolecules* **26,** 3062.

Eyler, R. W., Klug, E. D. and Diephuis, F. (1947) *Analyt. Chem.* **19**(1), 24.

Gautier, S. and Lecourtier, J. (1991) Polymer Bull. **26,** 457.

Glass, J. E. (1989) *Polymers in Aqueous Media—Performance through Associations*, Advances in Chemistry Series. American Chemical Society, Washington.

Hill, A., Candau, F. and Selb, J. (1993) *Macromolecules* **26,** 4521.

Inoue, Y. and Nagasawa, K. (1982) *Carbohydr. Res.* **111,** 113.

Jansen, E. (1918) German Patent 332,203; (1921) *Chem. Zentr.* **92**(2), 672.

Kricheldorf, H. R. (ed.) (1992) In *Handbook of Polymer Synthesis*, Part B, Chapter 25. Dekker, New York.

Landoll, L. M. (1989) In *Polymers in Aqueous Media—Performance through Associations*, Chapter 18—Advances in Chemistry Series. American Chemical Society, Washington, DC.

Magny, B., Illiopoulos, I. and Audebert, R. (1994) In *Macromolecular Complexes in Chemistry and Biology*, ed. Dubin, Bock, Davies, Schultz and Thies, Chapter 4. Springer-Verlag, Berlin.

McCormick, C. L., Bock, J. and Schultz, D. N. (1989) In *Encyclopedia of Polymer Science and Engineering*, Vol. 17, p. 730. Wiley & Sons, New York.

Mocanu, G., Carpov, A., Chapelle, S., Merle, L. and Muller, G. (1995) *Canadian J. Chem.*, **73,** 1933.

Picton, L., Mocanu, G., Mihaï, D., Carpov, A. and Muller, G. (1995) *Carbohydr. Polym.* **28,** 131.

Picton, L., Merle, L. and Muller, G. (1996) *Int. J. Polym. Analysis & Characterization* **2,** 103.

Rao, M. A., Walter, R. H. and Cooley, H. J. (1981) *J. Food Sci.* **46,** 896.

Reuben, J. and Conner, H. T. (1983) *Carbohydr. Res.* **115,** 1.

Rogovin, Z. A., Derevitskaya, V. A., Sun'Tun, C. W.-G. and Gal'Braikh, L. S. (1961) *J. Polym. Sci.* **53,** 117.

Roure, I., Boutebba, A., Milas, M. and Rinaudo, M. (1996) 14ème Colloque National de Chromatographie d'exclusion Stérique, Groupe Français des Polymères, Grenoble.

Strauss, U. P. and Jackson, E. G. (1951) *J. Polym. Sci.* **6,** 649.

Van der Horst, P. M., Batelaan, J. G. and Reuvers, B. (1994) Third International Workshop on Carbohydrates as Organic Raw Materials, Wageningen, The Netherlands, Azko Nobel patent No. PCT/EP94/00990.

Vogt, S., Heinze, T., Röttig, K. and Klemm, D. (1995) *Carbohydr. Res.* **266,** 315.

Wang, K. T., Illiopoulos, I., Audebert, R. (1991) In *Water Soluble Polymers*, ACS Symposium Series 467, eds S.W. Shalaby, C.L. McCormick and G.B. Bultler, American Chemical Society, Washington, DC.

Yalpani, M. (1988) In *Polysaccharides—Synthesis, Modification and Structure/Property Relations*, Chapter 7. Elsevier, New York.