

Effects of dispersed medium systems on substitution pattern and solution performance of carboxymethyl cellulose

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Abstract Effects of three dispersed medium systems consisting of isopropyl alcohol (IPA), ethyl alcohol (EtOH) and toluene (TOL) on the substitution patterns of carboxymethyl cellulose (CMC) were studied, and the corresponding influences on solution performances were investigated on a rheometer. In EtOH-IPA system, the structure of higher average substitution degree and enlarged partial substitution degrees disparity (determined by ¹H nuclear magnetic resonance) but lower distribution uniformity along molecular chains (speculated from static/dynamic light scattering) were characterized by which the thixotropy and apparent viscosity of solution decreased due to the aggregation of longer unsubstituted segments. For the phase separation (identified by gas chromatography) of TOL-IPA system, considerable unsubstituted regions in the structure aggregated into hydrophobic centers to form swollen macrogel particles in solution, leading to the sharp rise in apparent viscosity and almost constant flow-behavior index with hardly any thixotropic behaviors presented.

Keywords degree of substitution, alkalization, substitution uniformity, molecular interaction, aggregation

1 Introduction

Carboxymethyl cellulose (CMC) is a kind of polyanionic cellulose ether where carboxymethyl groups have been partly introduced along the cellulose backbones. In an aqueous medium, great impacts have been made by the electrostatic repulsive effects on the shapes and the interactions with water and other macromolecules of the

long-linear CMC molecules, from which high-level structure and considerable thickening ability are awarded [1]. By means of the excellent performances for fluid controlling and suspension stability as additives, CMC is widely used in coating, food, pharmaceutical, cosmetic and many other fields [2], especially applied as a framework material of gelatin explosive [3] and a binding agent of pasty propellant [4] in military areas.

The characteristics of CMC solutions have been widely studied so far, especially in aspects of viscosity, flowing behavior and thixotropy employing shear flow and dynamic tests as main methods. Many of these researches are based on the exterior factors such as concentration, temperature or shear rate [5–8], some of which have been developed quite deeply or precisely. For instance, according to the five states of macromolecular solutions divided by concentration [9], the investigation of abrupt changes in solution performances [10] and the foundation of mathematic models with higher universality across critical concentrations [11] have been explored. Take another example: for not accurately fitting the Ostwald-de Waele model generally utilized, the flow-behavior index of CMC solution may be toward to or even higher than 1 in some cases, the mechanism of which has been generally accepted as “flow-induced formation of macromolecular associations” [12] combined with the viscoelastic theories.

It is the molecular structure that determines the characteristics of CMC solution as an interior factor. For now, the achievements in this field have been mostly focused on molar mass with distribution [13–15]. As polymer electrolytes, the amount and distribution of ionic groups have significant influences on the inner structures of solutions through electrostatic repulsive effects [1]. However, no sufficient attention has been paid to the relationship of substitution patterns of carboxymethyl groups and performances of CMC solutions yet. Another important related subject is the skill for process control and

structural characterization. Although the technological process for CMC synthesis has been sufficiently improved, until now, the theoretical analysis about the various inner/outer factors on the chemical structures of productions [16–18] is not comprehensive and systematical enough, which is responsible for the shortage of precise controlling capacity. Among the characterizations of the CMC chemical structure, the distribution of carboxymethyl groups along the polymer chains has long been difficult, from which the capillary zone electrophoresis (CZE) matched with various detecting techniques has achieved great developments recently [19–21], not mature enough, but of bright future.

The scope of the present paper is to provide a specialized and systematical investigation of substitution patterns in CMC productions, including the reasons that cause disparities in degrees of substitution and distribution uniformity during the synthetic processes and the influences on molecular and aggregation structures as far as solution characteristics. To do so, three kinds of dispersed medium systems with different polarities and component compatibilities are employed, by which the corresponding CMC productions with almost identical molar mass but typical distinctions in substitution patterns are synthesized.

2 Materials and methods

2.1 Materials and sample preparation

The polymerization degree of cotton linters (M650) was 2200–2400. Other chemicals were of laboratory grade. The synthesis of CMC was carried out in a slurry system made up of dispersed medium and alkaline aqueous solution with monochloroacetic acid (MCA) as the etherifying agent. The dispersed medium was set as 50wt.%TOL-50wt.%IPA, 100wt.%IPA and 65wt.%EtOH-35wt.%IPA. Technological parameters were properly adjusted to keep M_w of all productions at the same level, determined by GPC to be 470000 (± 10000). Aqueous solutions of CMC were prepared by dissolving the appropriate amount of purified CMC powders in $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaCl solutions at room temperature. After moderate stirring for 6–24 h to clear up all the bubbles, sufficient time ($\geq 48 \text{ h}$) was allowed to achieve complete hydration. The concentrations for rheological and light scattering measurements were 1.5wt.% and $0.3 \text{ mg} \cdot \text{mL}^{-1}$, respectively.

2.2 Light scattering measurements

Static/dynamic light scattering (SLS/DLS) measurements were conducted on a laser light scattering system (Brookhaven, US) equipped with a BI-200SM goniometer and a BI-TurboCorr digital correlator. A solid-state laser polarized at vertical direction (GXL-III, 100 mW, CNI, China) operating at 532 nm was used as the light source.

SLS and DLS measurements were carried out at scattering angles in the range of 20° – 120° and $30^\circ/60^\circ/90^\circ$, respectively, the calculation methods of which were consulted from the literatures of Ji et al. [22] and Zhang et al. [23]. Sample solutions were prior filtered through disposable syringe filters (SFCA, nominal pore size: $0.45 \mu\text{m}$, Sartorius, Germany). All measurements were operated at $(25.00 \pm 0.01)^\circ\text{C}$.

2.3 Rheological measurements

Rheological measurements were conducted on a modular compact rheometer (MCR 300, Physica, Germany) equipped with a cylindrical geometry (diameter: 30 mm) at temperature of $(25.000 \pm 0.001)^\circ\text{C}$. In pseudoplasticity measurements, the shear rate was assigned in the range of 0.1 – 500 s^{-1} in 60 s. Pretreatment of recurrent shearing was carried out to remove the influences of thixotropic structures in solutions. In thixotropy measurements, the shear rate was assigned as “up-constant-down” mode in the range of 0.1 – 500 s^{-1} in 60 s for a single stage. Thixotropic index α was defined for thixotropy evaluation to avoid the interference of viscosity:

$$\alpha = \frac{S_U - S_D}{S_U} \times 100\% \quad (1)$$

where α was the thixotropic index (dimensionless), and S_U and S_D were the integral values of upward and downward flow curves ($\text{Pa} \cdot \text{s}^{-1}$), respectively.

2.4 Other measurements

^1H -NMR spectra were recorded with a superconductive nuclear magnetic resonance spectrometer (ARX 400, Bruker, Germany) scanning in the scope of 3.0–6.0 ppm ($1 \text{ ppm} = 10^{-6}$). The samples were prepared by dispersing CMC powders in D_2SO_4 - D_2O , followed by acidolysis at 90°C for 2 h. Cellulosic alkali adsorption in various dispersed medium was determined as reported by Bancroft and Calkin in Ref. [24]. Gas chromatography (GC) was conducted on a gas chromatograph (GC-7800, Purui, China) with a column of GDX-103. Temperature, bridge current and sample size were assigned as 100°C – 120°C , 120 mA and $1.0 \mu\text{L}$, respectively, with the hydrogen flow of 50 mL/min . Micrographs for solutions layers (thickness: 3.0 mm, 1.5wt.%) were pictured at 100 magnification on an optical inverted microscope (IX71, Olympus, Japan) equipped with a UIS2 optical imaging system at room temperature.

3 Results and discussion

3.1 Average/partial degree of substitution

According to the ^1H -NMR results, the average degrees of substitution (DS) of $\text{CMC}_{\text{TOL-IPA}}$, CMC_{IPA} and

$\text{CMC}_{\text{EtOH-IPA}}$ increase in sequence under the same reaction conditions (Table 1), which can be correlated with the polarity variations (TOL 2.4, IPA 3.9, EtOH 4.3) to indicate that the polarity enhancement of the dispersed medium contributes to the promotion of carboxymethylation. It is interpreted that the enhanced polar circumstance is not only in favor of the ion exchange interactions between MCA and NaOH but also promotes the migration of electron density distribution in $\text{Cl}-\text{C}$ covalent bonds toward Cl^- , so as to increase the reaction activity of the etherifying agents.

Table 1 Average/partial degrees of substitution determined by ^1H -NMR for CMC synthesized in various dispersed medium

Sample	Dispersed medium		Degree of substitution	
			DS	$x_2:x_3:x_6$
$\text{CMC}_{\text{TOL-IPA}}$	IPA:TOL	50wt.%;50wt.%	0.92	1.23:1:1.42
CMC_{IPA}	IPA	100wt.%	1.16	1.34:1:1.53
$\text{CMC}_{\text{EtOH-IPA}}$	IPA:EtOH	35wt.%;65wt.%	1.23	1.54:1:1.87

Due to the influences of steric effects and hydrogen bonds, the reaction activities of positions 2 and 6 in cellulose glucose residue units are higher than position 3. Moreover, the partial degree of substitution (x_i) at position 6 is higher than 2 instead if a relatively high liquid-solid ratio is applied. It is well known that the disparities of x_i at various positions become enlarged as DS increases within about 2.0; in particular, for DS in the range from 0.7 to 1.2, x_i at each position increases almost linearly [25]. However, as the present experimental results shown in Fig. 1, the disparities of x_i at various positions exhibit even a larger amplitude as DS increases, by which the curves tend to be divergent, deviating from the kinetic model of Spurlin [26] which has been demonstrated by Kulicke et al. as a theoretical prediction for x_i -DS relationships of CMC [25]. For the three samples referred to in the present work, x_i only shows linearity at position 2; whereas the substitution degree of $\text{CMC}_{\text{EtOH-IPA}}$ at position 3 even decreases slightly compared with CMC_{IPA} , indicating that a certain amount of carboxymethyl groups that should have substituted at position 3 turned to react at position 2 or 6 instead. This means that the enhanced polar circumstance drives the etherifying agents to attack hydroxyl positions with higher reaction activities. Consequently, the substitution pattern in glucose units of corresponding CMC production shows not only a higher reaction degree but also higher selectivity.

3.2 Substitution distribution uniformity

Figure 2 shows the light scattering results of CMC_{IPA} and $\text{CMC}_{\text{EtOH-IPA}}$ dilute solutions. From the line width distribution $G(\Gamma)$ curves in DLS measurements, it is obvious that the molecular size distribution of $\text{CMC}_{\text{EtOH-IPA}}$ moves toward lower values with various extents, depending on the measuring angles, compared

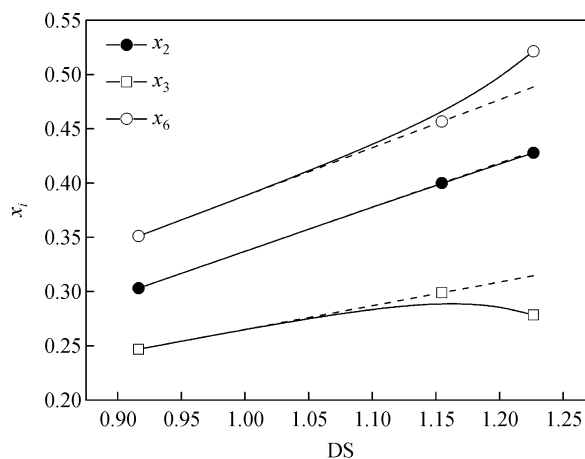


Fig. 1 Partial degree of substitution as a function of average degree of substitution for CMC synthesized in various dispersed medium, with the dash lines to illustrate the deviation of curves from the approximately linear relationship in this range

with CMC_{IPA} . Considering the contribution of DS to the increase of molecular hydrodynamic volumes [13], the drop of $\text{CMC}_{\text{EtOH-IPA}}$ molecular size can thus be attributed to the higher molecular curling extent. Forced by the heterogeneous electrostatic repulsions and steric effects determined by the low distribution uniformity of carboxymethyl groups along chains, the shape of $\text{CMC}_{\text{EtOH-IPA}}$ molecules represents to be locally extended and integrally curled, the influence of which even surpasses the changes in hydrodynamic volumes. This is in good accordance with the Z-averaged root-mean-square radius (R_g) results in SLS measurements. For the peculiar dissolving state of $\text{CMC}_{\text{TOL-IPA}}$ solution, the difficulties in filtering lead to certain influences on the DLS and SLS measuring results, respectively. Still, the R_g value of $\text{CMC}_{\text{TOL-IPA}}$ is evidently higher than other sample solutions, as shown in Table 2.

For the typical diphasic structure, the alkalization and etherification reactions mostly take place in amorphous regions of cellulose, being restricted by accessibility. Consequently, the substitution uniformity of carboxymethyl groups in CMC molecular chains primarily depends on the transition degree of crystalline regions of the cellulose in various dispersed media, which can be evaluated by cellulosic alkali adsorption (K_{AA}).

As results have shown, compared with IPA ($K_{\text{AA}} = 0.0473$), the cellulosic alkali adsorption in EtOH turns out to be lower ($K_{\text{AA}} = 0.0206$). In EtOH-IPA system, the reactions of etherifying agents and alkali cellulose show higher activities affected by the enhanced polar environment, but are concentrated in different regions for low K_{AA} , resulting in the molecular structure characteristics of higher DS and lower substitution uniformity along the polymer chains. Although the K_{AA} of TOL is close to EtOH ($K_{\text{AA}} = 0.0207$), distinct incompatibility of components is detected in TOL-IPA system. Determination results of GC for characteristic retention time are illustrated

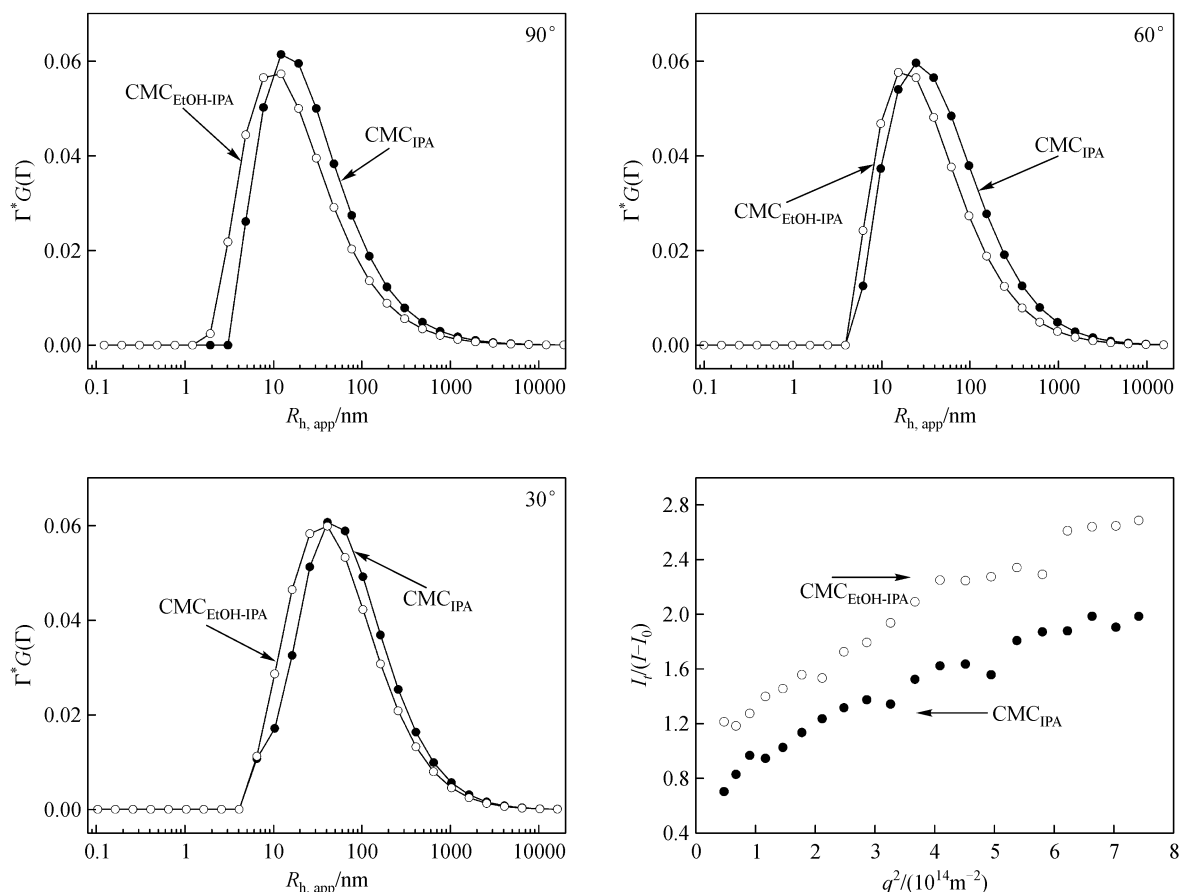


Fig. 2 Line width distribution, $G(\Gamma)$, in DLS and Z-averaged root-mean-square radius, R_g , in SLS measurements for CMC synthesized in various dispersed medium in $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaCl solution ($c = 0.3 \text{ mg} \cdot \text{mL}^{-1}$, $t = 25^\circ\text{C}$)

Table 2 Z-averaged root-mean-square radii with R -squares and characteristic/apparent molecular sizes by SLS/DLS for CMC synthesized in various dispersed medium^{a)}

Sample	SLS		DLS			
	R_g/nm	r^2	R_h/nm	$R_{h, \text{app}}(90^\circ)/\text{nm}$	$R_{h, \text{app}}(60^\circ)/\text{nm}$	$R_{h, \text{app}}(30^\circ)/\text{nm}$
CMC _{TOL-IPA}	113.39	0.9862	—	—	—	—
CMC _{IPA}	81.77	0.9778	46.5	16.6	26.0	35.2
CMC _{EtOH-IPA}	77.02	0.9853	43.4	10.3	20.6	30.0

a) The characteristic molecular size, R_h , is linearly extrapolated from the apparent molecular sizes ($R_{h, \text{app}}$) measured at scattering angles of $90^\circ/60^\circ/30^\circ$

below: phase separation can be observed by the addition of alkali (aqueous solution), most of which gathers in the aqueous phase (Fig. 3(a)); after MCA is added, a small quantity of organic phase is further separated from the bottom layer, and with the generated sodium chloroacetate (SMCA) richly concentrated (Fig. 3(b)). As can be seen, the contacts of reactants dispersed in TOL-IPA medium are highly discontinuous, accordingly causing the substitution pattern in the structure of CMC_{TOL-IPA} presents to be nonuniform, not only at molecular but also at the aggregative state level.

3.3 Performance of aqueous solution

The differences in the substitution pattern of carboxymethyl groups bring about changes in molecular interactions, which may further influence the performances of CMC aqueous solutions. Figure 4(a) shows the flow curves of various CMC sample solutions at different shear rates $\dot{\gamma}$ plotted over a double logarithmic scale. Compared with CMC_{IPA}, the apparent viscosity η of CMC_{TOL-IPA} and CMC_{EtOH-IPA} solutions presents obvious increase and decrease, respectively. Furthermore, the 2nd critical shear

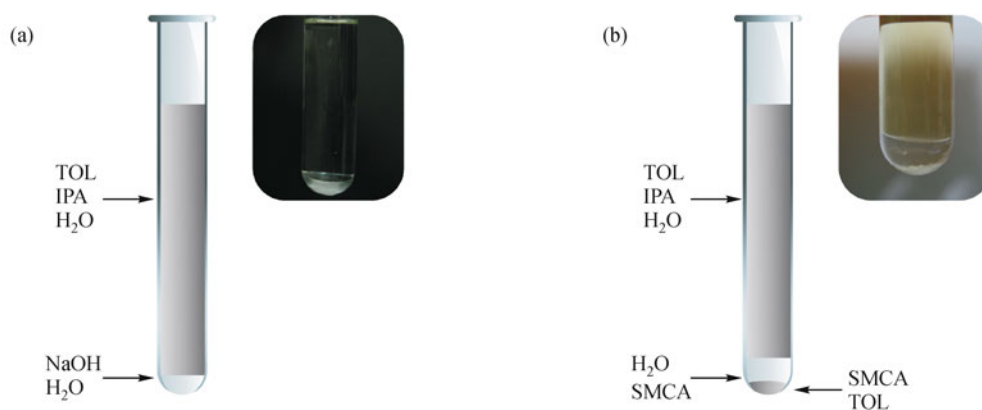


Fig. 3 Illustration of two/multi-phase separation in TOL-IPA system with addition of alkali and monochloroacetic acid (room temperature): **(a)** gathering of alkali in aqueous phase; **(b)** richly concentrated sodium chloroacetate in the further separated organic phase

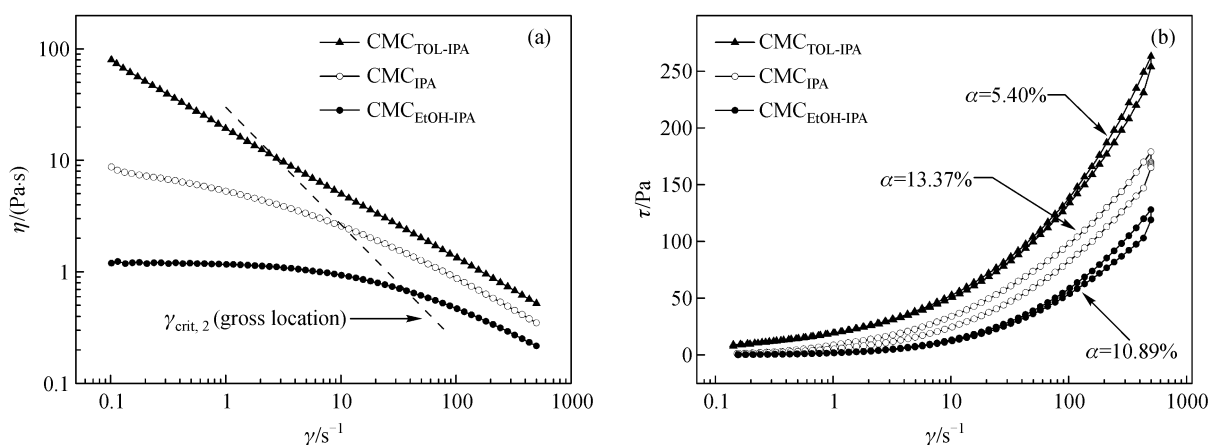


Fig. 4 Effects of dispersed medium on the rheological performances of CMC in $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaCl solution ($c = 1.5\%$, $t = 25^\circ\text{C}$): **(a)** apparent viscosity as a function of shear rate with 2nd critical shear rate marked; **(b)** hysteresis loops with thixotropic index indicated

rate, $\gamma_{\text{crit}, 2}$ [10], can be clearly observed from the η - γ curve of $\text{CMC}_{\text{EtOH-IPA}}$ solution, indicating that the weaker but similar molecular interaction pattern to CMC_{IPA} still exists; while in $\text{CMC}_{\text{TOL-IPA}}$ solution, the flowing behavior represents to highly correspond with a power law model in the full range of shear rates, which suggests that no essential effects to the inner structure can ever be made by shear forces. As seen in Fig. 4(b), via the “up-constant-down” shearing process, CMC_{IPA} solution exhibits more obvious thixotropic properties, with the highest thixotropic index α value. The thixotropy of $\text{CMC}_{\text{EtOH-IPA}}$ solution declines to some extent accompanied with the reduction of apparent viscosity. As to $\text{CMC}_{\text{TOL-IPA}}$ solution, however, hardly any thixotropic behaviors can be observed, with the lowest α value, although its apparent viscosity turns out to be considerably high.

Acting as entangled, overlapped coils in aqueous solutions, CMC molecules form irregular network structures through interactions. The rises in degrees of

substitution and distribution uniformity of carboxymethyl groups are advantageous to increasing the active links among the molecular chains, by which a higher-level structure and higher apparent viscosity can be acquired in the DS range of present work with molar mass equivalent. Meanwhile, the recovery process of solution under persistent shearing becomes more time-dependent after the internal structure is being destroyed, showing pronounced thixotropic properties (Fig. 5(a)).

The unsubstituted segments or glucose residues in CMC molecules have the tendency of reciprocally binding with various levels in solutions [27]. In EtOH-IPA system, for the higher discrete degree of etherification zones in cellulose, longer unsubstituted segments may be arranged in molecular chains, resulting in the fact that certain amounts of molecules approach mutually and keep away from others, by which the configuration of aggregating units with a relatively discrete distribution in solution is formed, which not only causes the weakening of the

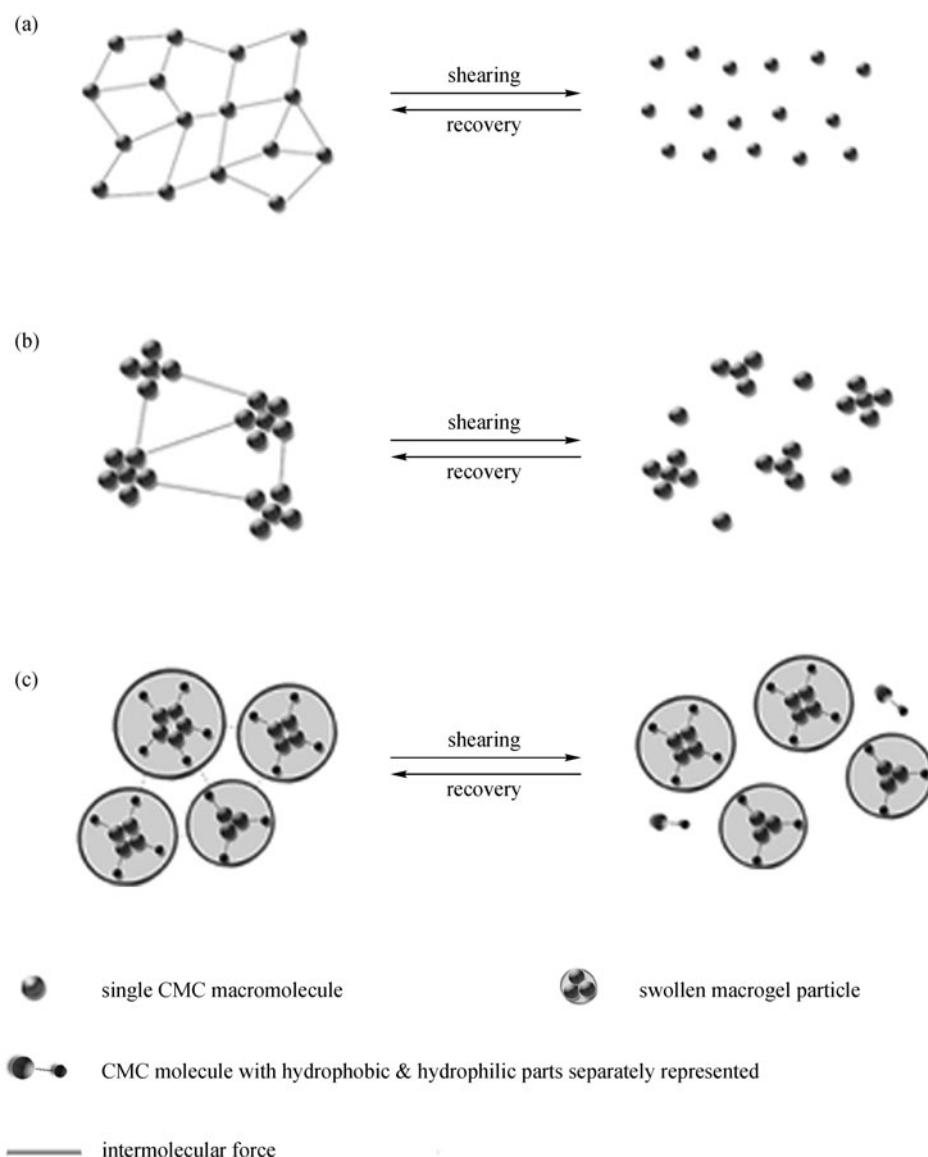


Fig. 5 Illustration of molecular interaction patterns for CMC synthesized in various dispersed medium in 0.1 mol·L⁻¹ NaCl solution during the shearing and recovery processes ($c = 1.5\%$, $t = 25^\circ\text{C}$): **(a)** compact network structure with molecular active links; **(b)** weakened network structure with molecular aggregating units; **(c)** tightly and independently arranged swollen macrogel particles

network structure and the corresponding viscosity reduction but also, on the other side, integrally brings down the recovery extent of the solution structure under shear forces, leading to the decline of time dependence and thixotropy (Fig. 5(b)).

Even through various solubilization treatments (shearing, heating or shaking, e.g.), CMC_{TOL-IPA} is unable to sufficiently dissolve in aqueous medium, which is inconsistent with regular laws of the same DS productions [28]. This is mainly because of the component incompatibility in TOL-IPA system. Due to the phase separation (Fig. 3), the highly inhomogeneous alkalization at the aggregative state level leads to the considerable unsub-

stituted regions in cellulosic structures with fairly low hydration capacity, which aggregate into hydrophobic centers coated by the hydrophilic parts through hydrogen bonds with water molecules, so as to form highly swollen macrogel particles [29], tightly and independently arranged in solution. It is this special structure that determines the high apparent viscosity of CMC_{TOL-IPA} solution and the dynamic characteristics partly similar to weak gel [30]. Furthermore, for the structure of solution undergoing shear actions only changes in the dispersion degree of gel particles, almost no time dependence or thixotropic behaviors are exhibited (Fig. 5(c)).

The different solution morphologies due to the

disparities in substitution patterns of carboxymethyl groups can be explicitly observed, as depicted in Fig. 6, from the various solution layers conducted on an optical microscope.

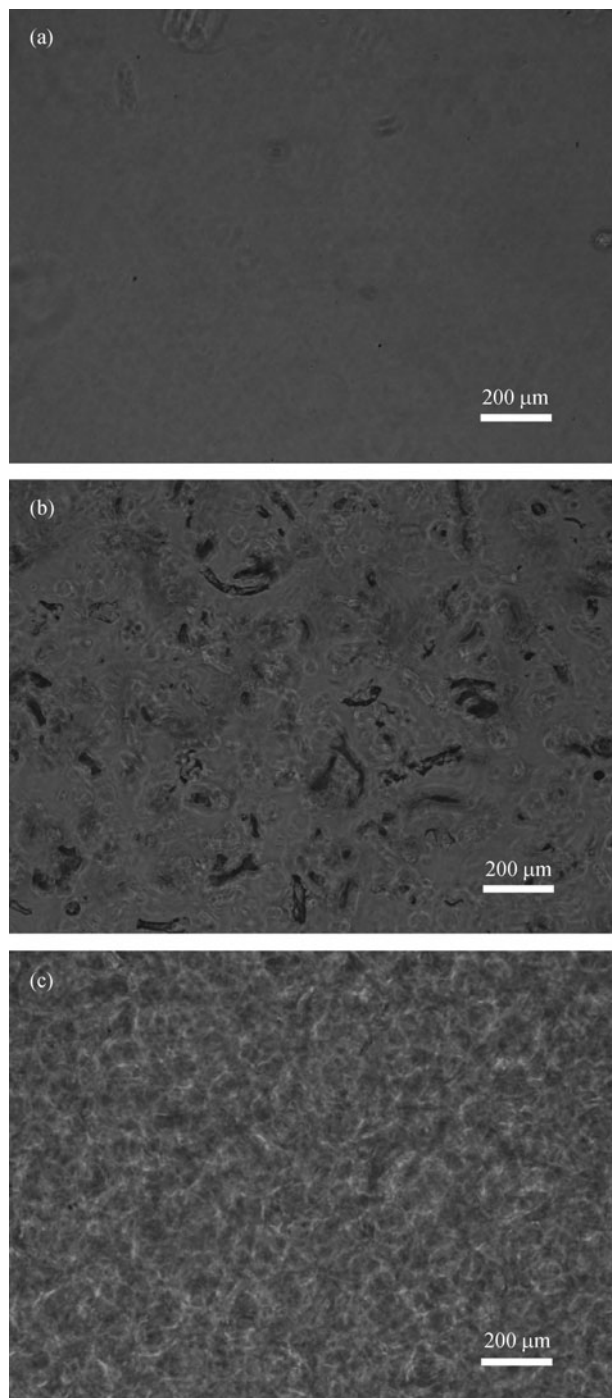


Fig. 6 Typical images of layer appearances for CMC synthesized in various dispersed medium in $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaCl solution ($c = 1.5\%$, room temperature): (a) CMC_{IPA} ; (b) $\text{CMC}_{\text{EtOH-IPA}}$; (c) $\text{CMC}_{\text{TOL-IPA}}$

4 Conclusions

Influences of three dispersed medium systems on the substitution patterns of CMC productions with identical M_w were studied. $^1\text{H-NMR}$, DLS/SLS and GC results showed that the differences in basification were the root causes to the structural disparities at the molecular and aggregative state level. Apparent viscosity, flowing behavior and thixotropy properties of sample solutions were further analyzed with reasons interpreted. It was concluded that:

1) Enhanced polarity of dispersed medium was of advantage to increasing the reaction capacity of the etherifying agents, resulting in higher selectivities to the hydroxyl positions and degrees of substitution.

2) Alkali adsorption and component compatibility of the dispersed medium made impacts upon the distribution uniformity of substitution along molecular chains or even enlarged to regions. With certain amounts of long unsubstituted chain segments but sufficient hydration capacity, the molecules tended to reciprocally aggregate and integrally weaken the network structure, causing decrease in apparent viscosity and thixotropy.

3) As the substitution nonuniformity reached a certain degree at the aggregative state level, sharp rise and drop in apparent viscosity and thixotropy, respectively, and a flowing behavior highly corresponding with the power law model were shown due to the forming of swollen macrogel particles centered on the gathering of the hydrophobic regions.

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