Aqueous Viscosity Enhancement through Helical Inclusion Complex Cross-Linking of a Hydrophobically-Modified, Water-Soluble, Cationic Cellulose Ether by Amylose

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Received April 23, 1997; Revised Manuscript Received June 30, 1997[⊗]

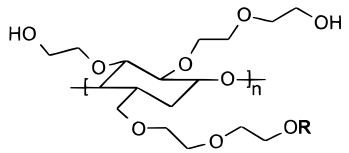
ABSTRACT: It has been found that combinations of a hydrophobically-modified, water-soluble, cationic cellulose ether, **3**, and amylose (a linear polysaccharide isolated from potato starch) dissolved together in water at high temperature and carefully cooled afford increased solution viscosity over either polymer acting alone. The mode of viscosity enhancement has been attributed to formation of a cross-linked network created when the amylose forms a noncovalent, helical clathrate with the hydrophobic groups attached to **3**. Such an effect is not observed when **3** is replaced with a nonhydrophobic, water-soluble, cationic cellulose ether, **2**, or when the amylose is replaced with either amylopectin or α-, *β*-, or *γ*-cyclodextrin. The resulting noncovalent, cross-linked clathrate network is pseudoplastic and temperature unstable. Heating the complex results in complete loss of solution viscosity, which then gradually rebuilds as the solution is recooled.

Introduction

It is now generally accepted, on the basis of pioneering results demonstrating formation of helical inclusion complexes between amylose and iodine, and amylose and fatty acids, that amylose, a nearly linear, water-soluble polysaccharide containing α-D-1,4-anhydroglucose units, is capable of forming helical inclusion complexes with a variety of organic substrates.[1,2] The helical coil formed by the amylose/lipid inclusion complex in aqueous solution has been demonstrated to comprise from 6 to 8 repeating glucose units per helical turn. X-ray diffraction analysis indicates the helix twists in a left-handed direction referred to as an α-helix and assumes a V-type crystal structure when complexed with aliphatic molecules.[3,4] The aliphatic moiety, within this intermolecular relationship, inserts itself into the lipophilic interior of the amylose helix. The amylose is often referred to as the host and the molecule the amylose wraps itself around is the guest in this arrangement. The variability in the number of glucose units in the helix suggests the helix must be able to expand or contract as necessary to accommodate the size of the guest.[5,6]

Indeed, such helical configurations most likely account for the availability of α-6-, *β*-7-, and *γ*-8-cyclodextrins, which are ring-closed cycloamyloses biologically derived from potato starch.[7] Cyclodextrins, because they are cyclic structures, unlike linear amylose, have well-defined sizes and assume a toroidal shape with the size of the cyclodextrin determined at the larger opening of the toroid. The interior diameter of α-cyclodextrin, for example, is approximately 4.9 Å, while the exterior diameter is approximately 14.6 Å.

Cyclodextrins are commercially available and have been shown to form a plethora of inclusion complexes (clathrates) with various organic guests. The complexation of cyclodextrins with fatty acids has been explored in detail.[8] Calculations indicate that complexation of alkyl groups with cyclodextrins occurs primarily through the wider opening of the toroid.[9] It has been recently observed that viologen polymers, cationic polymers having poly(paraquat−octamethylene) groups, can form inclusion complexes with α-cyclodextrins.[10]



(**1**) **R**=H
(**2**) **R**=$CH_2CH(OH)CH_2N(CH_3)_3Cl$
(**3**) **R**=$CH_2CH(OH)CH_2N(CH_3)_2(CH_2)_{11}CH_3Cl$

Figure 1. Idealized structures for **1**−**3**.

Cellulose, another naturally occurring polysaccharide, is a linear diastereomeric allotroph of amylose composed of repeating *β*-D-1,4-anhydroglucose units. However, unlike amylose, the change in stereochemical configuration renders cellulose water-insoluble.[11] Cellulose can be made water-soluble by graft reaction with ethylene oxide. The resulting poly[*β*-D-1,4-anhydroglucose-*g*-oxyethylene] is referred to as hydroxyethylcellulose (HEC), **1**, Figure 1. HEC can be made cationic by reaction with (2,3-epoxypropyl)trimethylammonium chloride, **2**.[12] In addition, HEC can be rendered both cationic and hydrophobic by reaction with (3-chloro-2-hydroxypropyl)-*N*,*N*-dimethyl-*N*-dodecylammonium chloride, **3**.[13]

Several recent papers addressed the interaction of starch with hydrophobically modified synthetic polymers such as poly(ethylene-*co*-acrylic acid), telechelic poly(*ϵ*-caprolactone) phosphate, and hydrophobically-modified poly(vinyl alcohol), (HMPVA).[14−16] In particular, the authors investigating aqueous solutions of HMPVA demonstrated viscosity enhancement when starch was blended at relatively high weight fractions with poly(vinyl alcohol) derivatized with a dodecyl hydrophobe.[16]

These authors attributed this viscosity enhancement to specific interactions between the amylopectin portion of the starch and the dodecyl groups attached to the poly(vinyl alcohol). Amylopectin is a highly branched, high molecular weight portion of starch composed of linear α-D-1,4-anhydroglucose units that contain branching α-D-1,4-anhydroglucose units attached to the main chain through α-D-1,6-anhydroglucose linkages. The

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[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1997.

S0024-9297(97)00554-8 CCC: $14.00

authors suggested the specific interaction was most likely a helical clathrate between the amylopectin and the dodecyl groups on the HMPVA. The existence of a helical complex between amylopectin and fatty acid moieties has been speculated upon, but no direct evidence exists for such a complex.[6,17,18]

Noncovalent cross-linking of **2** and **3** has been reported to occur in the presence of various anionic and cationic surfactants.[19−22] Aqueous solution viscosity maximums are reported to occur at the critical micelle concentration (cmc) of the surfactant where the cationic polysaccharides apparently cross-link through electrostatic interaction with the surfactant polar headgroups. Nonionic surfactants do not effect such viscosity enhancements.[20] Recent work suggesting that minor covalent cross-linking of hydrophobically modified poly(alkylmethyldiallylammonium bromide)s affords increased aqueous solution viscosity for these cationic "polysoaps" led us to believe the dodecyl hydrophobes of **3** might complex with various hosts, resulting in an enhancement of the aqueous viscosity of solutions containing **3**.[23] We report, at this time, that this is indeed the case when amylose is employed as the host.

Experimental Section

Materials. Guest Polymers. Poly[β-D-1,4-anhydroglucose-*g*-oxyethylene-*g*-(2′-hydroxypropyl)-*N*,*N*,*N*-trimethylammonium chloride] (UCARE Polymer JR), **2**, and poly[β-D-1,4-anhydroglucose-*g*-oxyethylene-*g*-(2′-hydroxypropyl)-*N*,*N*-dimethyl-*N*-dodecylammonium chloride] (Quatrisoft Polymer LM-200), **3**, were obtained from Amerchol Corp. (Edison, NJ) and were used without further purification. The exact molar substitution levels of ethylene oxide reported for **2** and **3** are typically 2.5−2.8, as reported in the patent literature, and the molar substitution levels of cationic nitrogen for **2** and **3**, which can be determined by Kjeadahl analysis, were found to be 0.45 and 0.1, respectively. The molecular weight of **2** is approximately 400 000 while the molecular weight of **3** is approximately 175 000, both molecular weights being determined by the intrinsic viscosity of their unmodified HEC starting materials prior to the cationization reaction.

Host Polymers. Potato amylose, potato amylopectin, and γ-cyclodextrin, were obtained from Sigma (St. Louis, MO). The amylopectin and γ-cyclodextrin were used without further purification. The amylose was further purified to remove residual butanol by extraction in a Soxhlet extractor with 95% aqueous 2-propanol for 24 h and subsequent drying to constant weight in a vacuum Abderhalden at 85 °C. The molecular weight of the amylose was determined to be approximately 800 000 by GPC analysis on an Ultrahydrogel column using pullulan standards. This is in close agreement to recently reported values for potato amylose molecular weight.[24] α- and β-cyclodextrin were obtained from Pfanstiehl Laboratories, Inc. (Waukegan, IL) and were used as received. In all cases, the equilibrium moisture of the polymers was determined using a Denver Instrument model IR-100 moisture balance and the weights of the polymers were adjusted to compensate for the moisture content. Turbidity measurements were run using a Monitek model 21 nephelometer at 25 °C.

Rapid Inclusion Formation and Viscosity Measurement, Method A. Solutions of the guest polymers, **2** and **3**, were prepared by thoroughly dissolving a known amount of the cellulose ether into a known weight of distilled water at 25 °C. Solutions of the hosts were prepared by placing the required weight of the host in a threaded pressure tube (Ace Glass, Vineland, NJ), adding distilled water as required, and sealing the tube with a teflon O-ring and stopper. The vessel was heated to 100 °C for 20 min (except for amylose, which was heated to 120 °C for 1 h) and cooled to 90 °C. Microscopic examination of these solutions showed no apparent undispersed fragments of amylose or amylopectin.

A known weight of the hot host solution was quickly transferred to the guest solution where it was intimately blended with stirring for 5 min. The resulting mixture was then allowed to stand at room temperature without stirring for 1 h. A portion of the mixture was transferred to a sample chamber of a Brookfield UL Adapter, and the sample was allowed to equilibrate at 25 °C for 15 min prior to obtaining a reading. The viscosity was measured using a #00 spindle on a Brookfield model DV-II+ viscometer at 25 °C (unless otherwise indicated).

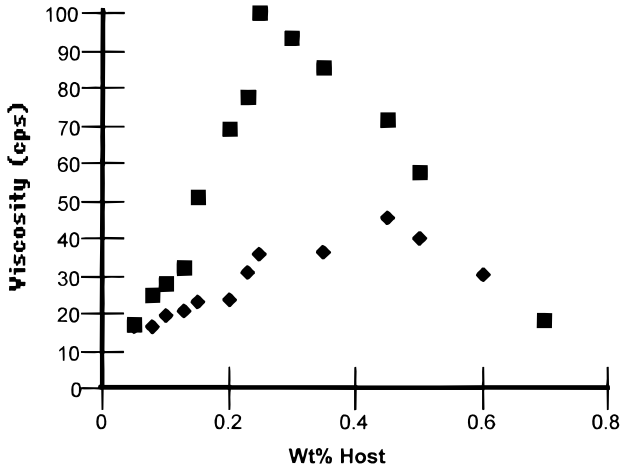

Figure 2. Plot of viscosity (cps) versus wt % amylose (■) and wt % amylopectin (◆) with 1 wt % **3** prepared following method A, taken at 6 rpm and 25 °C.

Slow Inclusion Formation and Viscosity Measurement, Method B. Aqueous solutions of the guest polymers, **2** and **3**, were prepared by dissolving a known amount of the cellulose ether into a known weight of distilled water and heating to 90 °C. The host samples were prepared as described above. When both the hot guest and hot host solutions were ready, the necessary weight of the guest solution was transferred to a beaker equipped with magnetic stirring. To this solution was added the required weight of the host solution and the mixture was allowed to stir for 5 min to intimately mix both polymers. The contents of the beaker were transferred to a threaded glass pressure tube and the mixture was returned to a 90 °C water bath. The sample was allowed to cool slowly for 24 h without stirring by shutting off the power to the waterbath. The viscosity of the mixture was measured as described above.

Results and Discussion

Aqueous solutions of 1 wt % **3** were prepared, following method A, in which increasing weight percentages of amylose and amylopectin were added. The viscosity of each solution was measured, and the results are shown in Figure 2. It appeared from this initial screening that some type of viscosity enhancement might be occurring at approximately 0.25 wt % amylose and 0.45 wt % amylopectin, although the magnitude of the effect was lower for the amylopectin. To assure ourselve that this apparent viscosity enhancement was not the result of amylose or amylopectin retrogradation, we ran viscosity control experiments for amylose and amylopectin up to 1% concentration without addition of **3**. The solution viscosity for both hosts up to 1% solids remained below 40 cps, regardless of the polymer concentration.

Having established a rudimentary level of amylose and amylopectin that showed the greatest viscosity improvements, aqueous solutions were prepared by following method B with 1 wt % **3** and either 0.25 wt % amylose or 0.45 wt % amylopectin. It has been shown in the literature that amylose inclusion complexes formed in a rapidly cooled fashion tend to have greater random coil distribution, while those formed in a more

Table 1. Solution Viscosity Data for Inclusion Complexes of 1 wt % 3 and either 0.25 wt % Amylose or 0.45 wt % Amylopectin Prepared Using Methods A and B

host	guest	method	viscosity[a] (cps)
amylose	**3**	A	175
amylose	**3**	B	810
amylopectin	**3**	A	46
amylopectin	**3**	B	45

[a] Viscosities of amylose samples were taken at 0.6 rpm at 25 °C. Viscosities of amylopectin samples were taken at 6.0 rpm and 25 °C.

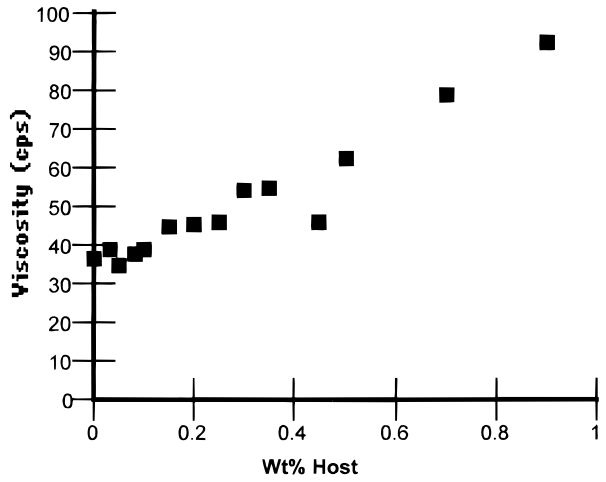

Figure 3. Plot of viscosity (cps) versus wt % amylose with 1 wt % **2** taken at 6.0 rpm and 25 °C following method A.

slowly cooled fashion have greater crystallinity and are consequently more thermodynamically stable.[25] The sample of 1 wt % **3** and 0.25 wt % amylose prepared by method B showed a nearly 5-fold increase in viscosity compared to the corresponding sample prepared by method A, Table 1. The comparable sample of 1 wt % **3** and 0.45 wt % amylopectin prepared by method B did not show such a pronounced viscosity increase.

The mode of viscosity enhancement does not appear to be some type of unusual electrostatic interaction occurring between the amylose and the cationic charge of **3.** To substantiate this, we ran 1 wt % solutions of **2** with increasing amounts of amylose following the procedure described in method A, Figure 3. No significant viscosity increase was noted that could not be attributed to the increase in amylose concentration. Samples were also prepared in which the solution of amylose and the solution of **3** were prepared, cooled, and then mixed. No viscosity increases were noted in these examples. We feel that while it is known that potato amylose is randomly substituted with small amounts of anionic phosphate ester groups, the mechanism of viscosity enhancement is not related to formation of a polyelectrolyte complex. One might expect that such a complex would also form between amylose and **2** (which has even greater cationic character) or should occur on mixing cooled solutions of amylose and **3**. This is not the case, and the complexation in this situation is clearly temperature dependent. The viscosifying effect is also most likely not a manifestation of the molecular weight difference between **2** and **3**. Polysaccharide **2** actually has a higher molecular weight than **3**. Thus, one would expect the higher molecular weight polysaccharide would afford the correspondingly higher solution viscosity if chain entanglement were the sole mode of polysaccharide interaction.[26]

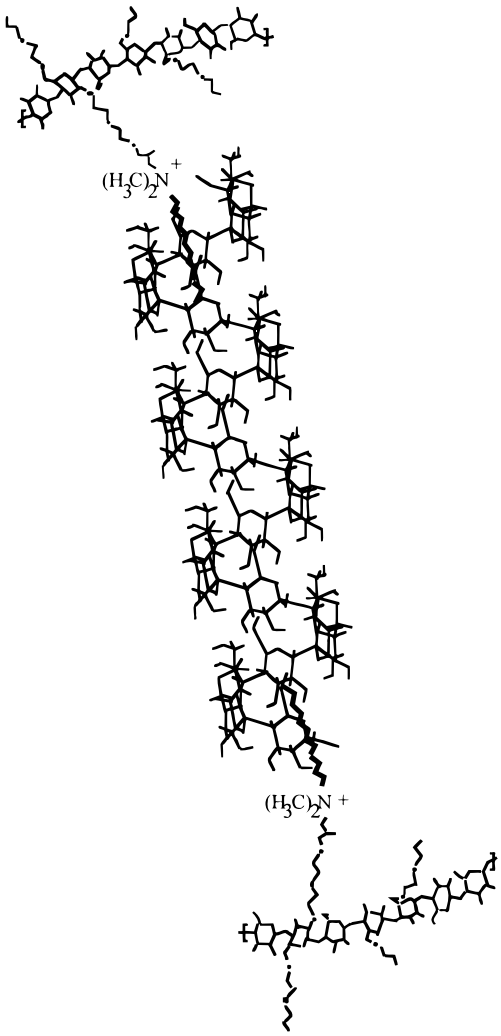

Figure 4. Proposed helical cross-linking mechanism for **3** and amylose.

It becomes apparent from the data shown for a combination of **3** and amylose dissolved in water at a weight ratio of approximately 4:1 and slowly cooled that some type of interaction must be occurring. We feel that the most probable mechanism of interaction is formation of a helical, cross-linking clathrate between the amylose and hydrophobic groups on **3**, Figure 4. This is consistent with prior observations for inclusion complexes between amylose and fatty acids and is supported by recent work demonstrating that a single amylose molecule is capable of forming a dual inclusion clathrate with two molecules of palmitic acid.[27] It has recently been suggested that cationic charge on the hydrophobe might further help to stabilize the amylose clathrate.[28] The complexation, in our example, leads to an approximately 5-fold increase in solution viscosity.

We examined the effect of other hosts known to complex fatty alkyl groups through internal complexation. Mixtures of **3** and α-, β-, and γ-cyclodextrins were prepared following method A, Figure 5. It appears, from the results, that these hosts actually suppress the solution viscosity of **3**. This behavior has been previously observed when cyclodextrins are added to solutions of hydrophobically-modified HEC used to thicken paint and has been attributed to a blocking effect wherein the cyclodextrin actually prevents the hydrophobic moieties from interacting in solution.[29]

The complex formed between **3** and amylose has pseudoplastic rheology, Figure 6. This would be ex-

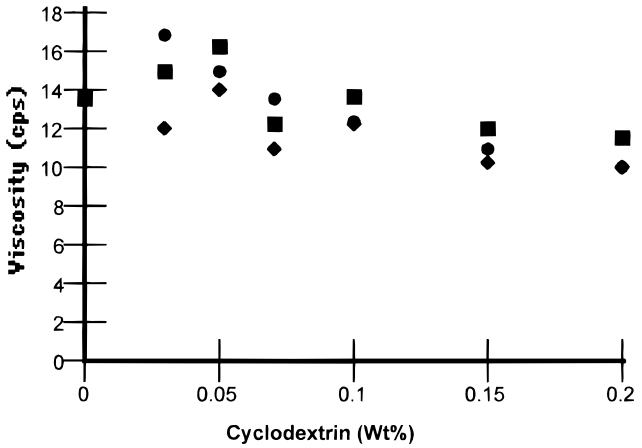

Figure 5. Plot of viscosity versus wt % α- (■), β- (◆), and (●) γ-cyclodextrin with 1 wt % **3** prepared following method A, taken at 6 rpm at 25 °C.

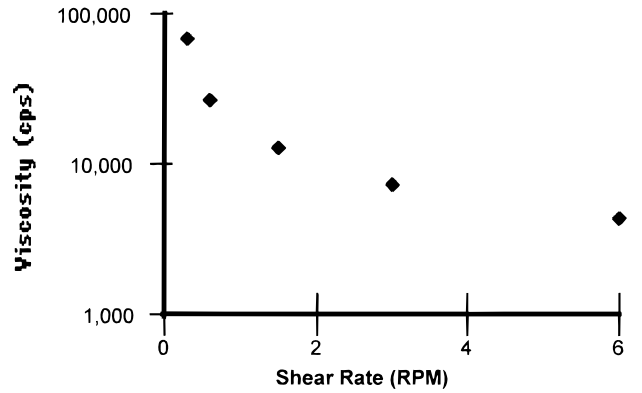

Figure 6. Log of viscosity (cps) versus shear rate (rpm) for 1 wt % **3** and 0.25 wt % amylose solution prepared by method B (LV #2 spindle, 25 °C).

pected if the mechanism of thickening involved a helical complex. The springlike amylose would expand when placed under a shearing force, without releasing its lipophilic guest, and it would return to its original coiled state after the shear force was removed. Similar behavior for coiled polymers has been recently used to explain the adhesive forces that exist in polymeric bacterial adhesion pili.[30]

Additional rheological characterization needs to be completed before we can conclusively state whether the complex is indeed a gel, although the solution's appearance is gellike. A solution of 1.0 wt % **3**, 0.25 wt % amylose, and 98.75 wt % water, prepared by method B, can be made to extend nearly 1 in. from a container when it is carefully poured, and yet, it "snaps back" into the container when it is returned to an upright position. Such behavior is impossible for either polymer alone at these concentrations.

It appears from the data shown in Figure 7 that the cross-linked complex is thermally unstable. The viscosity diminishes as the mixture of **3** and amylose is slowly heated from 30 to 90 °C. The viscosity of the complex at 90 °C is equivalent to the viscosity of a 1 wt % solution of **3** at 90 °C. This is consistent with the temperature at which amylose is known to be completely thermally uncoiled. The viscosity again increases as the solution is slowly recooled, returning to its original value within 24 h at 30 °C.

The accumulated data on the aqueous solution viscosity increase, which occurs when amylose is added to solutions of **3**, are consistent with the proposed cross-

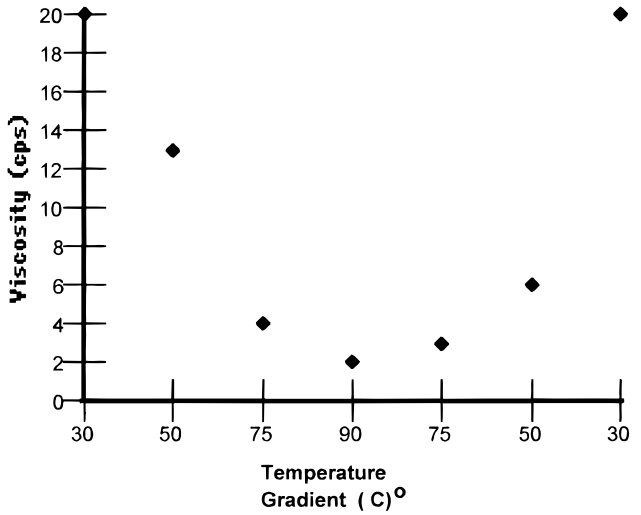

Figure 7. Effect of temperature (°C) on viscosity (cps) of a 1 wt % **3** and 0.25 wt % amylose complex prepared by method B taken at 6 rpm.

Table 2. Turbidity Measurements (in NTUs) for the Guest, 3 (1.0 wt %), the Host, Amylose (0.25 wt %), and the Complex of Guest and Host (1.0 wt %/0.25 wt %) in Water Prepared by Method B

polymer solution	turbidity (NTUs), 24 h	turbidity (NTUs), 60 h
amylose	44	>200
3	4	7
amylose/**3**	162	152

linking mechanism. Cationic cellulose polymers **2** and **3** have similar levels of poly(oxyethylene) grafting, while **3** actually has less cationic substitution than **2**. Cationic polysaccharide **3** also has a lower molecular weight than **2**, as reported previously. Therefore, it is unlikely that the observed viscosity enhancement is the result of some artifact of any of these characteristic differences between these two guests. The only other significant difference between these polymers resides in the lipophilic dodecyl group on the quaternary ammonium nitrogen of **3**.

The possibility of the viscosity enhancement being attributed to polymeric phase separation has been suggested. Unaided and microscopic visual inspection of the complex does not reveal any signs of apparent phase separation in the complex. However, visual inspection can be misleading in this type of polymer system. To try to further examine the possibility of phase separation, we conducted turbidity measurements on solutions of the guest (1.0 wt %), the host (0.25 wt %), and the complexed combination of both (1.0/0.25 wt %) at 24 and 60 h, Table 2.

Interestingly, the turbidity data taken at 24 h indicate that the complex is more turbid than either polymer solution alone. This might have suggested that phase separation is occurring. However, when the samples were allowed to sit undisturbed for 60 h, the turbidity of the amylose solution increased significantly (it could not be measured with our available equipment). This is the result of amylose retrogradation. Retrogradation occurs when chains of amylose in solution wrap around themselves as double helices, forming colloidal crystallites.[31] The turbidity of the combined solution, however, did not change significantly. This suggests to us that retrogradation of the amylose in the presence of the cationic hydrophobic polymer is interrupted because the amylose is tied up with the hydrophobe complex. The

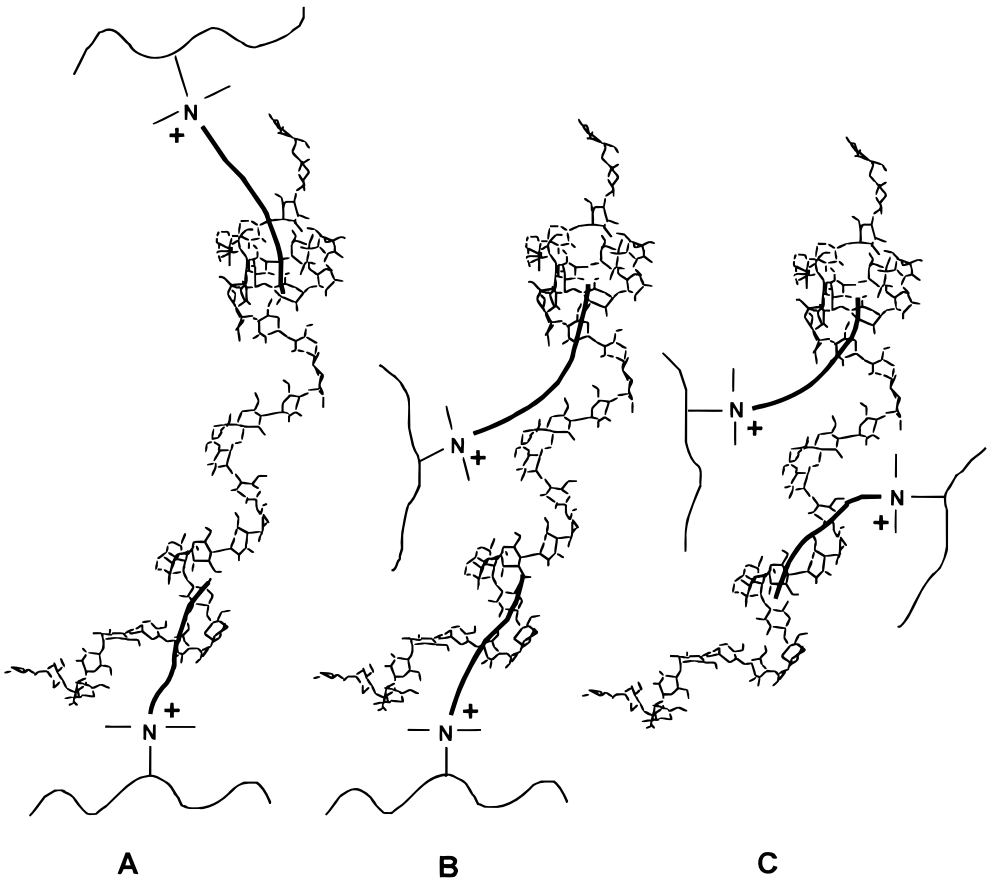

Figure 8. Possible mechanisms of Quatrisoft hydrophobe cross-linking with amylose: (A) tail-to-tail; (B) head-to-tail; (C) head-to-head.

turbidity measurements appear to lend further support to the complexation mechanism.

Using the available data for the molar substitution levels of the cationic, hydrophobic moiety on **3**, the cationic polysaccharide's molecular weight of 175 000, and the measured molecular weight for amylose of 800 000, and calculating at the optimum weight percent ratio of **3**:amylose of 4:1, one finds that the molar stoichiometry of hydrophobic groups to amylose is approximately 1.7:1, a very close approximation to the ideal value of 2:1 one might expect to find if the inclusion complex cross-linking mechanism is occurring. We are attempting, at this time, to further confirm this gelation mechanism by in-depth NOESY NMR spectroscopy. We hope to report on these studies in the near future.

We have indicated a tail-to-tail relationship between the two dodecyl clathrates in the proposed cross-linking mechanism shown in Figure 4. However, several possible arrangements could be responsible for the observed viscosity increase, Figure 8.

We cannot rule out any of these possible relationships at this time, but the tail-to-tail cross-linking would appear to minimize the degree of cationic and lipophilic repulsion between the guests.

The lack of solution vicosity enhancement seen when the various cyclodextrins are employed as hosts is not surprising. Generally speaking, the inclusion clathrate between cyclodextrins and fatty acids involves insertion of the hydrophobic fatty acid tail into the larger opening of the cyclodextin toroid. Insertion of a fatty acid chain into the tighter opening of the toroid, or dual insertion of two hydrophobes into the wider cyclodextrin opening is energetically unfavorable, but it would be required in order for the cyclodextrins to work as cross-linking agents.

Finally, although we cannot conclusively rule out helical complex formation between **3** and low concentrations of amylopectin, our data suggest that if inclusion does occur, either it is only a weak interaction in this particular example or the highly branched nature of amylopectin disrupts the cross-linking viscosity enhancement. This directly contradicts the results discussed by the authors examining solutions of HMPVA where the viscosity enhancement in their system occurs only in the presence of high concentrations of amylopectin, not amylose as demonstrated above.[16]

Conclusion

The study of the interesting physicochemical behavior of the various components of starch continues to attract widespread attention. We have demonstrated that the helix formed by amylose, the linear component of starch, is a dynamic entity capable of expanding and contracting to accept more than one guest in a single helix. The consequences of this unique behavior can create a cross-linked network with a hydrophobically-modified, cationic polymer, **3**. The structure of the complex of **3** and amylose bears a strong resemblance to an idealized Maxwell dashpot.[32] Additional investigation needs to be carried out to fully verify the mechanism of complexation, and other intriguing aspects of this unique rheological behavior will be reported in the near future.

Acknowledgment. The authors would like to thank Des Goddard, Lisa Bouldin, Emmett Partian, and David Donabedian for their helpful comments and discussion.

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MA970554V