Macromolecules **1995,** *28,* 1704−1708

Notes

Uptake of Sodium Dodecylbenzenesulfonate by Poly(*N*-isopropylacrylamide) Gel and Effect of Surfactant Uptake on the Volume-Phase Transition

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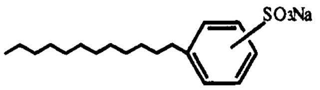
Received June 2, 1994

Revised Manuscript Received December 6, 1994

Introduction

Several recent studies have focused on the effects of surfactants on the swelling equilibrium of polymer gels from both fundamental[1−6] and technological[7,8] standpoints. We have demonstrated that ionic surfactants such as sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium chloride (DTAC) affect the thermally induced volume-phase transition of a nonionic *N*-isopropylacrylamide gel (NIPA gel);[4] both transition temperature and volume jump during the transition increase remarkably with increasing SDS or DTAC concentration. These results have previously been explained by assuming that the surfactant molecules adhere to the nonionic NIPA gel through hydrophobic interaction, by means of which adhesion the gel is converted into an ionic gel. Conductivity measurements for aqueous surfactant solutions in the presence and absence of the gels as a function of temperature support this assumption.[4] However, none of the previous works[3,4] dealing with systems consisting of ionic surfactants and nonionic gels, including our own conductometric study, have yet reported on details of the nature of the binding of surfactants to gel networks.

In this study, we attempted to perform quantitative measurements of the uptake (or adsorption) of surfactant molecules by NIPA gels and to explain the effect of surfactant binding on the phase transitions of the gels. Investigations on this subject not only will serve to enhance our understanding of the structure of surfactant-bound ionic NIPA gels but will also provide information about possible technological applications of surfactant-modified hydrogels in actuators, sensors, superabsorbers, and so on. Sodium dodecylbenzenesulfonate (NaDBS) was selected as the surfactant used in this study due to its possession of a UV absorption band at ca. 220 nm which permits a highly accurate determination of the difference in the amounts present before and after uptake during the measurements.



NaDBS

Experimental Section

Materials. NaDBS was purchased from Tokyo Kasei Kogyo, Ltd., Tokyo, Japan. All of the chemicals for the preparations of the gels and homopolymers of NIPA were the same as those used in the previous study.[4]

Preparation of Gels. Cylindrical and cubic gels were used to measure the swelling curves and NaDBS uptake, respectively. Preparation was carried out at 0 °C by gelling the desired amounts of an aqueous monomer solution containing NIPA (700 mM), *N,N'*-methylenebisacrylamide (cross-linker; 8.6 mM), *N,N,N',N'*-tetramethylethylenediamine (accelerator; 0.001% v/v), and ammonium persulfate (initiator; 3.5 mM). The cylindrical gel (0.065 ± 0.002 mm inner diameter and 0.74 ± 0.06 mm length) was obtained in a test tube into which capillaries had been inserted prior to the gelation of the monomer solution. The cubic gel, with sides of 5 ± 1 mm each, was prepared by gelling the monomer solution in a glass container, followed by the cutting of the gel into fixed-size segments with a slicer.

Preparation of the NIPA Homopolymer. The polymerization of NIPA was carried out by stirring a methanol solution (100 mL) containing the monomer (10 g) and α,α'-azobis(isobutyronitrile) (initiator; 100 mg) at 60 °C for 1 h under nitrogen. The polymer obtained was purified in the same manner as described in the previous paper.[4]

Swelling Curves. The cylindrical gel was inserted into a water-jacketed glass cell and its size and shape were monitored and analyzed using an AVEC image processor (Hamamatsu Photonics, Model C1966). The temperature was controlled to within a range of ±0.1 °C using a temperature control system with water circulating around the cell containing the gel samples.

NaDBS Uptake. The lyophilized cubic gels (0.8 g) were put into a measuring flask and swelled to the required size with a small amount of distilled water. After the addition of the required amount of NaDBS solution into the flask, the volume of the aqueous phase containing the gels was precisely adjusted to 40 mL using distilled water. The flask was allowed to stand for 50 h at 25 °C and then for more than 200 h at the required temperatures. The NaDBS concentration of supernatant liquid after the incubation was spectrophotometrically determined from a calibration curve showing the relationship between NaDBS concentration and absorbance at 220 nm.

Cloud Point Measurements. The cloud points of aqueous solutions of NIPA polymer in the presence and absence of NaDBS were measured using a spectrophotometer (Shimadzu Model UV-240) equipped with a thermocontrol apparatus (Shimadzu SPR-5/KPC-5 system). The polymer concentration was fixed at 0.2% w/v throughout the measurements.

Results and Discussion

Changes in Swelling Curve and Transition Temperature. Figure 1 shows the swelling curves of NIPA gels as a function of NaDBS concentration. The curves were expressed using the ratio of the gel diameters normalized by the fully collapsed diameter ($D_{\text{collapsed}}$). In the absence of NaDBS, NIPA gels were swollen at

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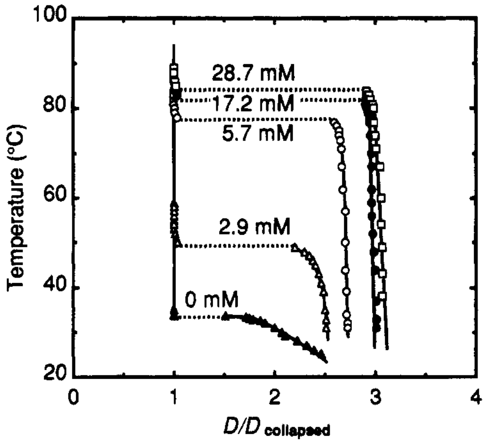

Figure 1. Temperature dependence of equilibrium gel diameter as a function of NaDBS concentration. The surfactant concentrations are shown in the figure. The diameters (D) are normalized using the fully collapsed diameter ($D_{\mathrm{collapsed}}$).

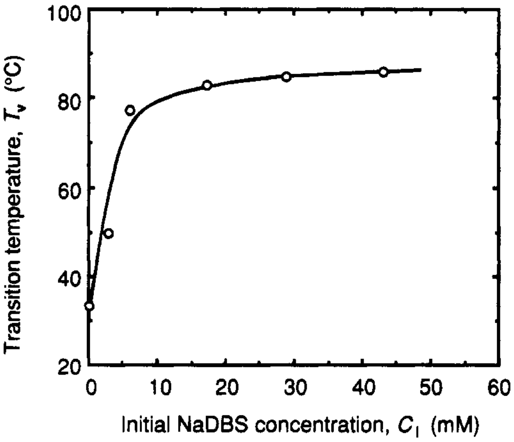

Figure 2. Effect of NaDBS concentration on transition temperature (T_v).

lower temperatures and underwent a discontinuous volume-phase transition (collapse) at 33.6 °C; the volume change at this temperature was about 8 times the fully collapsed volume. In the presence of NaDBS, both the volume-phase transition temperature (T_v) and the net volume change at the transition increased with increasing surfactant concentration. These aspects of the swelling curves are consistent with those of our previous study[4] regarding the effects of ionic surfactants such as SDS and DTAC on the volume-phase transition of NIPA gels. Thus, the results for NaDBS can also be interpreted in a qualitative way as follows: NaDBS molecules are bound to the polymer networks of the NIPA gel through hydrophobic interaction, by which the nonionic gel is converted into an ionic gel with a high transition temperature and a large volume.

The effect of NaDBS on the swelling behavior of NIPA gels was further studied by examining the change in T_v with surfactant concentration (Figure 2). NaDBS brought about an initial increase in T_v up to a certain concentration; increasing the concentration of NaDBS further produced negligible effects on T_v, which thus could be considered as having reached a plateau beyond a characteristic concentration (~20 mM for NaDBS in this study; ~20 mM for SDS and ~16 mM for DTAC in the previous study[4]). These characteristic concentrations, which are likely to resemble one another independent of species, were considerably higher than the critical micelle concentrations (C_{cmc}) of NaDBS (ca. 1.2 mM at room temperature) and SDS (8.1–8.3 mM at room temperature) and also slightly higher than the C_{cmc} of DTAC (ca. 14 mM at room temperature). This important feature in the swelling behavior of NIPA gels in the presence of ionic surfactants is discussed below in terms of the nature of the binding of the surfactants to gel networks.

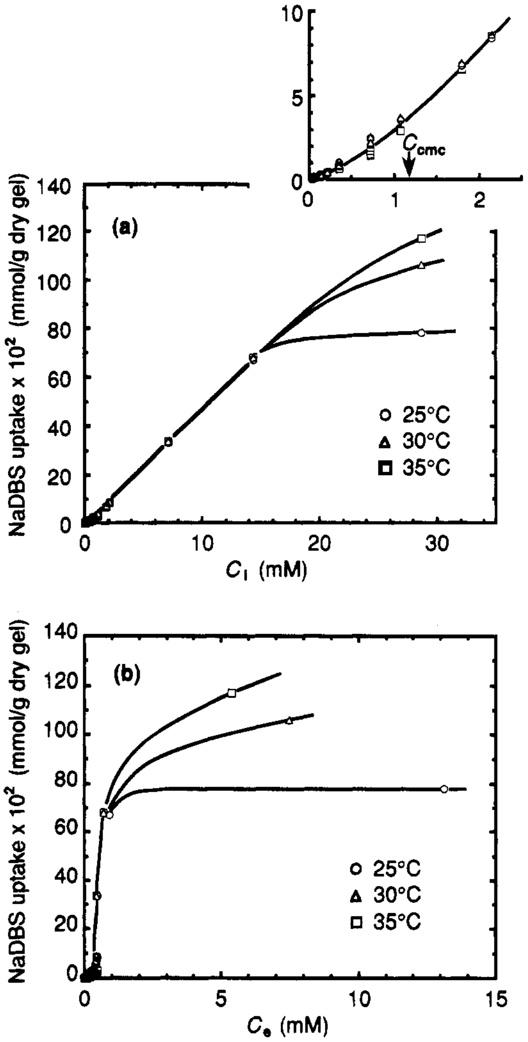

Figure 3. Dependence of surfactant uptake by NIPA gel on initial NaDBS concentration (C_i) (a) and equilibrium NaDBS concentration (C_e) (b) at different temperatures.

NaDBS Uptake by NIPA Gel. An understanding of surfactant effects on the swelling behavior of NIPA gels can be provided by quantitative measurements of surfactant binding to the polymer networks of the gel. Therefore, the uptake of NaDBS by gels was studied at 25, 30, and 35 °C for a wide range of NaDBS concentrations involving the C_{cmc}. The experimental results obtained were then analyzed by plotting the amount of NaDBS uptake against the initial concentration (C_i) (Figure 3a) and the equilibrium concentration (C_e) (Figure 3b). The surfactant uptake increased almost linearly with an increase in C_i at $C_i < 16$ mM passing through the C_{cmc}, and at 25 °C the uptake leveled off in the range of $C_i > 16$ mM. In addition, the temperature had very little influence on the uptake at $C_i < 16$ mM. In this concentration range, it was found from the plots of the uptake against C_e that most of the initially added NaDBS molecules were bound to the gel with remaining trace amounts in the supernatant solution.

The adsorption isotherm, obtained by plotting the amount adsorbed against the equilibrium concentration,

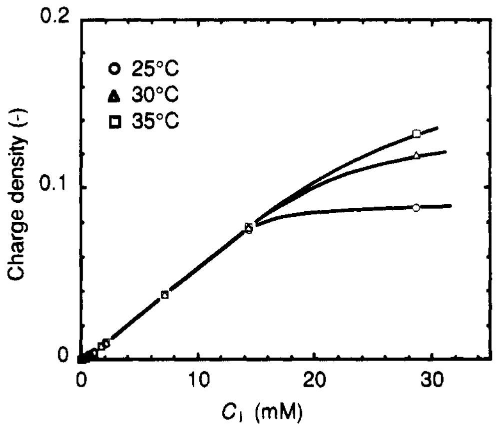

Figure 4. Dependence of overall charge density of NaDBS-bound NIPA gels on initial surfactant concentration (C_i) at different temperatures.

is a useful tool for estimating the affinity between adsorbent and adsorptive. In the case in which adsorption is governed by the highest affinity, in the adsorption of polycations from water onto anionic colloids via electrostatic interaction,[9] for example, the equilibrium concentration is zero until all the adsorption sites are saturated with adsorbents, after which the adsorption amount reaches a constant value. The results in Figure 3b seem to be very close to these aspects, especially at 25 °C. As a result, it can be said that the NaDBS molecule with the hydrophobic dodecylbenzene group binds strongly to the hydrophobic parts of the polymer networks in the NIPA gel. Moreover, such strong binding through the hydrophobic interaction is not affected by the C_{cmc} of NaDBS, since Figure 3a shows that the surfactant uptake increased linearly at $C_i < 16$ mM without passing through a specific inflection point or plateau. Thus, we believe that a strong hydrophobic interaction between NaDBS molecules and NIPA gels enables the surfactant to bind to the polymer networks not only from free NaDBS molecules but also from micelles of these, though the destruction or breakdown of the latter (see ref 10).

Change in Charge Density of NIPA Gel Caused by NaDBS Uptake. The "overall" charge density expressed in moles of bound NaDBS per mole of monomer units in the gel was calculated from the results in Figure 3a and plotted against C_i. The moles of monomer units in the gel were then obtained by dividing the dry gel weight by the molecular weight of the NIPA monomer, since the moles of *N,N'*-methylenebisacrylamide forming cross-linking points in the gel are less than 8% of the total monomer residues, the influence of which is negligibly small during the calculation of the moles of monomer units in the gel. The results obtained are shown in Figure 4, from which a maximum overall charge density of 0.135 was found under the conditions used ($C_i = 28.7$ mM; 35 °C).

Such a NaDBS-bound NIPA gel seems to correspond to an ionic gel which can be prepared by substituting about 14% of the NIPA monomers (700 mM in the present polymerization) with ionic monomers such as sodium acrylate. Thus, it is of interest to compare the swelling curves for NaDBS-bound and sodium acrylate-copolymerized NIPA gels with the same charge density. The previous study[11] of a spherical copolymer gel consisting of NIPA (82%) and sodium acrylate (18%) measured the T_v values to be 60 °C (shrinking process) and 50 °C (swelling process) in pure water. These T_v values are lower than that for the NaDBS-bound gel (82 °C), although the charge density of the copolymer gel was slightly larger than that of the NaDBS-bound gel. In contrast, the volume change at the T_v (60 °C) for the copolymer gel was much larger (372 times the fully collapsed volume) than that for the NaDBS-bound gel (27 times the fully collapsed volume at $T_v = 86$ °C).

Questions have been raised as to why the NaDBS-bound ionic NIPA gel exhibited a volume change smaller than that of the copolymer gel with a similar charge density and why the T_v of the former was higher than that of the latter. The answer to these questions would help clarify the nature of surfactant-bound gels. In order to discuss this subject, we now assume that surfactant molecules bind only to the polymer networks within a layer (or part) of the gel near to the surface, but not to all of the networks within the body of the gel. This is because negative charges of the surfactant-bound layer seem to hinder the further diffusion into internal parts of the gel of the surfactant molecules with charges of the same sign. Under such an assumption, it is reasonable to expect that some part of the highly ionized polymer network in the NaDBS-bound gel has a net charge density much larger than the "overall" density shown in Figure 4, thereby showing a T_v value higher than that for the copolymer gel. However, the charge density of the internal part of the surfactant-bound gel is very low or close to zero, resulting in the volume collapse of this domain at temperatures > 33.6 °C (i.e., T_v of NIPA gels in pure water). As a result, the surfactant-bound gel is composed of a highly ionized swollen part and a very slightly ionized (or nonionized) collapsed part at temperatures > 33.6 °C. Therefore, the total change in the gel volume at T_v for the surfactant-bound gel was smaller than that for the copolymer gel.

Assuming a local binding of surfactants also makes it possible for us to answer why the curves for T_v vs surfactant concentration for NaDBS, SDS, and DTAC leveled off at a similar concentration unrelated to the C_{cmc}. This is because the surfactant binding in the vicinity of the gel surface may become saturated at a certain concentration, the level of which is independent of the kind of ionic surfactant when (a) the dimensions of the layer with the bound surfactant are much smaller than that of the sample gels and (b) all of the surfactants used have the same binding affinities toward the gel.

Binding Number of NaDBS to the Polymer Networks. A more quantitative analysis of NaDBS uptake by NIPA gels allows an estimation of the binding number (n) of the surfactants, through the study of which we may obtain information about the local binding of surfactants. The n value may be estimated by considering the following equilibrium reaction:

$$nS + G = S_nG \tag{1}$$

where S, G, and S_nG denote the surfactant, gel, and gel with surfactants, respectively. The equilibrium constant (K) can be then defined as

$$K = \frac{[S_nG]}{[S]^n[G]} \tag{2}$$

where the brackets signify the equilibrium concentration of the species. Taking into account the fact that the degree of saturation (Y) of surfactant binding is given by

$$Y = \frac{[S_nG]}{[S_nG] + [G]} \qquad (3)$$

and also that [S] = C_e, we obtain the following relation which is useful in determining the n and K values (see ref 12):

$$\log\left(\frac{Y}{1-Y}\right) = n \log C_e + \log K \qquad (4)$$

In order to estimate the n value from the plots of log[$Y/(1 - Y)$] vs log[S] using eq 4, we have to define the total number of the NaDBS binding sites within the gel. However, there is no well-defined criterion for determining the binding sites in the case in which NaDBS is bound to NIPA gels through hydrophobic interaction, although the total number of binding sites within polyelectrolyte gels, such as an ion exchanger, can be defined on the basis of the content of ionizable groups. Thus we first considered the total number of binding sites to be the total of the NIPA monomer units in the gel, by assuming a 1:1 stoichiometric association of NaDBS with the monomer residues within the gel (method A). Under this assumption, Y in eq 3 is equivalent to the charge density calculated in the previous section. Another method (method B) for estimating total binding sites is an experimental determination taking the uptake at C_i = 28.7 mM and 25 °C to represent the saturated amount of NaDBS binding. Figure 5 shows the plots of log[$Y/(1 - Y)$] vs log[S] obtained from the data for the NaDBS uptakes at C_i < 16 mM using both analytical methods. All of the plots are straight lines with correlation coefficients of 0.937–0.964. The n values estimated by means of the slope of each straight line were 2.7–2.0 (method A) and 3.0 (method B), from which we can say that more than two molecules of NaDBS were bound to one binding site in the gel. Nevertheless, the charge density at C_i < 16 mM was less than 0.1, and under such conditions the charge density or uptake at 25 °C leveled off. These results evidently indicate that the surfactant molecules bind only to the polymer networks lying near to the gel surface but not to all of the networks in the body of the gel.

Effect of NaDBS Concentration on Cloud Point of NIPA Solution. There are factors common to the volume-phase transition of NIPA gel and the phase separation of NIPA polymer solution. Thus, the comparison of the surfactant effects on both phenomena would provide clues for examining the local binding of NaDBS to the gel. Figure 6 shows the dependence of the phase separation temperature (i.e., cloud point, T_c) on NaDBS concentration, from which a rise in T_c with increasing NaDBS concentration was observed. Our previous conductometric study[4] has demonstrated that SDS is bound not only to the cross-linked NIPA chains in the gel but also to homopolymer chains of NIPA in an aqueous solution through hydrophobic interaction. In addition, the SDS binding to NIPA polymer was quantitative when different amounts of the polymer were added in a surfactant solution with a cosntant SDS concentration. Taking these into account, the rise in T_c observed in Figure 6 can be understood as a result of the increase in the ionizable group content of NIPA polymers caused by the NaDBS binding—in other words, the inhibition of temperature-induced association between NaDBS-bound NIPA polymers in an aqueous solution which is due to overcoming hydrophobic interaction by electrostatic force.

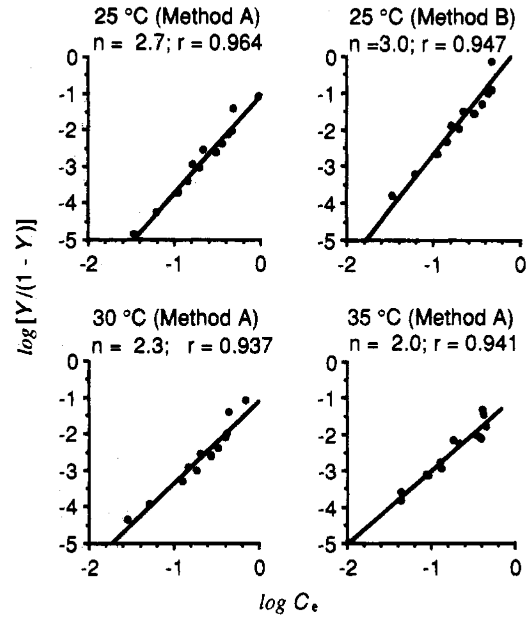

Figure 5. Logarithmic plots of [$Y/(1 - Y)$] against C_e at different temperatures obtained by analytical methods A and B. The binding numbers (n) of surfactants and the correlation coefficients (r) are shown in each plot.

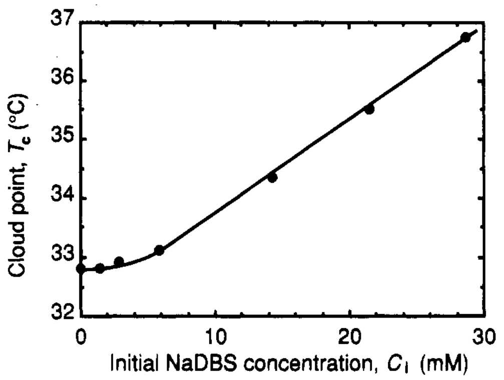

Figure 6. Change in cloud point (T_c) with initial surfactant concentration (C_i) for aqueous NIPA polymer solutions containing different amounts of NaDBS.

There remains the unsolved question of the difference in the structures of the NIPA chains with the bound NaDBS molecules between the gel and polymer solution; thus, a direct comparison of the T_c and T_v values at the same surfactant concentration may not be valid at the present stage. However, the T_c was less than 37 °C even at a very high NaDBS concentration of 29 mM, the value of which was much lower than the T_v in Figure 2. Even if this unsolved question is taken into consideration, the large observed difference between the T_c and T_v could be discussed in connection with the difference in the modes of NaDBS binding to the NIPA chains within the gel and solution; that is, the surfactant binding in the polymer solution should have been a homogeneous change, whereas it took place heterogeneously in the part of the gel near the surface.

Conclusion

It has become apparent that NaDBS binds to the networks in the near vicinity of the surface but not within the body of NIPA gel through hydrophobic interaction, converting the gel into an ionic gel (see ref 13). The hydrophobic interaction is fairly strong; as a result, the micelles of NaDBS formed at concentrations above the critical micelle concentration are destroyed during the process of the binding of the surfactant to the gel. Such surfactant binding brings about a local increase in the charge density of the gel. Thus, NaDBS-bound ionic NIPA gels exhibit an increase in phase transition temperature accompanied by an increase in gel volume, the aspects of which are different from usual polyelectrolyte gels with a similar charge density, such as a copolymer gel consisting of NIPA and sodium acrylate. Such ionic gels will prove to be of interest in technological applications due to the heterogeneously ionzied layer(s) of networks which exist within them.

Acknowledgment. We wish to thank R. Craig and R. Martin for their critical reading of the manuscript. This research was supported by a grant from the New Energy and Industrial Technology Development Organization (NEDO), Japan.

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(10) It may not be reasonable to consider micelles as being bounddirecty to the polymer networks within the gel, because their surfaces are covered with hydrophilic ionizable groups.

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(12) Although the temperature dependence of K seems to provide useful information about the local binding of surfactants, there are many difficulties involved in its estimation and discussion. This is because (i) we can compare K values only when n is independent of temperature, (ii) K should vary depending upon the criterion for determining binding site, and (iii) it may be very hard to distinguish how K is affected by surfactant–polymer interaction and surfactant–surfactant interaction. Thus, we did not try to estimate or discuss the K values on the basis of data on NaDBS uptake using eq 4.

(13) During the revision of this paper, we carried out a new experiment based on the staining of the surfactant molecules bound to the NIPA gel. It was observed that only the parts of NaDBS-bound gels in the near vicinity of their surfaces are stained with cationic dyes such as Crystal Violet and Methylene Blue. In contrast, the internal part of a surfactant-bound gel and the whole of a surfactant-free gel are stain-free. These results provide direct evidence that the surfactant molecules bind only to the polymer networks lying near the gel surfaces. More systematic and detailed studies using staining methods will be reported elsewhere in the very near future.

MA9412703