Differential Scanning Calorimetry, Rheology, X-ray, and NMR of Very Concentrated Agarose Gels†

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ABSTRACT: Some physicochemical properties of very concentrated agarose gels were examined in order to clarify the relation between their structure and properties and the role of water in gelation. E' increased slightly up to a certain temperature T_c and then decreased with increasing temperature. T_c was shifted to higher temperatures with increasing concentration. The temperature dependence of the elastic modulus was discussed on the basis of a statistical treatment proposed previously. The upper limit of the number of segments which reel out from junction zones seemed to increase with increasing concentration. The concentration dependence of the elastic modulus was examined by using a cascade theory. From the curve fitting, the functionality was found to be 25. Proton spin–lattice relaxation time T_1 decreased with increasing concentration of gels, but this decreasing tendency became less apparent beyond 25% concentration. An endothermic DSC peak was observed at about 75 °C, which shifted slightly to higher temperatures with increasing concentration. Endothermic enthalpy determined from the area under the endothermic peak was approximately proportional to the concentration. X-ray diffraction and scanning electron microscopic observations were also carried out. Both these structural studies together with rheological studies suggested that junction zones in concentrated agarose gels are crystalline; i.e., helical chain segments are aggregated. It appears that the structure of the ordered regions in the present (lower molecular weight) agarose gels changes at 25% concentration.

Introduction

Because of its importance as a typical model for gelling materials, or as a texture modifier in the food industry, or as a bacterial medium in the biomedical field, many investigations have been published that aim at clarifying the gelation mechanism of agarose.[1-4] All these investigations have been concerned with dilute gels. However, the structure and properties of concentrated gels are important from the practical point of view. In addition to this, the structure is expected to tend to a more crystalline state in very concentrated gels. Recently, we reported some physicochemical properties of concentrated agarose gels up to 18% (w/w).[5] In this paper, we report dynamic Young's modulus E', DSC, X-ray analysis, and NMR for very concentrated agarose gels up to 40% (w/w).

Experimental Section

Materials. One kilogram of the sea weed *Gelidium amansii*, produced in August 1984 in the Izu Suzaki region (Japan), was suspended in 1.5 L of a 3% (w/w) aqueous sodium hydroxide solution. This was heated with 1.5 L of water, and the extraction of the polysaccharide was carried out by autoclaving at 130 °C. The agarose was isolated from each extract by the method described previously.[6] The final yield (weight of each sample) was about 20 g. About 70 g of agarose was obtained by repeating this procedure. The pH of the extracts ranged from 6 to 7. Each extract was left at room temperature to form a gel, and the gel was cut into strings and kept frozen for about 15 h. The frozen preparations were thawed in running water and dried in vacuo at 40 °C. The intrinsic viscosity in 0.01 mol/L aqueous sodium thiocyanate solution at 35 °C was 1.7 dL/g. The content of 3,6-anhydro-L-galactose was 43.0%, and that of sulfate ester was 0.0011 mol/$C_6H_{10}O_5$.

The dried specimens were swollen in water at 40 °C overnight, preheated at 75 ± 5 °C for 30 min, and then heated at 105 °C for a time from 10–15 min, using an autoclave. The solutions obtained were placed into a mold to give a cylindrical shape for viscoelastic measurements. The gels were stored at 4 °C for a week to mature and then kept at the measuring temperature for 1 h before the measurements.

Measurements. The dynamic modulus E' and the mechanical loss tangent tan δ were measured at a constant frequency of 2.5 Hz by a Rheolograph Gel (Toyo Seiki Seisakusho). Details of the measurements of E' and tan δ were described elsewhere.[5,6]

The DSC measurement was carried out by the use of a sensitive DSC SSC 560U (Seiko Instruments & Electronics Ltd.). Forty milligrams each of agarose gels was sealed into silver pans of 70 μL. Distilled water was used as a reference material and the weight was made to be equal (within 0.1 mg) to that of the sample, in order to obtain a flat base line. The heating or cooling rates were 2 °C/min. X-ray diffraction measurements were performed with a scintillation counter using Cu Kα radiation operated at 40 kV and 40 mA through a graphite monochromator. The apparatus used in this study was Geigerflex Rad IIB (Rigaku Denki).

NMR measurements were carried out by using a JEOL-JNM-FX90A FT-NMR apparatus with ^1H = 90 MHz at 26 °C. The sample gel was sealed in an NMR tube of 5-mm diameter. The spin–lattice relaxation time T_1 was determined by Fourier transformation of the accumulated FID signal by the inversion-recovery method. The spin–spin relaxation time T_2 was determined by the spin–echo method.

Scanning electron micrographic observation was done by the same method reported previously[7] using a Hitachi HSM-2B SEM. The acceleration voltage was 25 kV, the electric current was 1.0 × 10^{11} A, and the magnification was 15 000. The sample gel was frozen by using liquid nitrogen and then broken into small pieces. Then, water was extracted from the pieces by methanol, and finally gold was coated onto their surfaces.

Results and Discussion

Elastic Modulus. The temperature dependence of the dynamic modulus E' for agarose gels of various concentrations is shown in Figure 1. E' increased slightly up to about t_1 = 35 °C and then began to decrease with increasing temperature. Beyond t_2 (about 45 °C), it decreased quite rapidly with increasing temperature. The temperature t_1 or t_2 seemed to increase slightly with increasing concentration. E' began to decrease at 35 °C for a 3% gel. The temperature dependence of such a thermoreversible gel has been explained on the basis of a model consisting of junction zones (somewhat crystalline regions) and flexible chains which connect the junction zones.[8] The flexible chains were assumed to be Langevin chains, i.e., the ratio of the end-to-end distance of the chain to the

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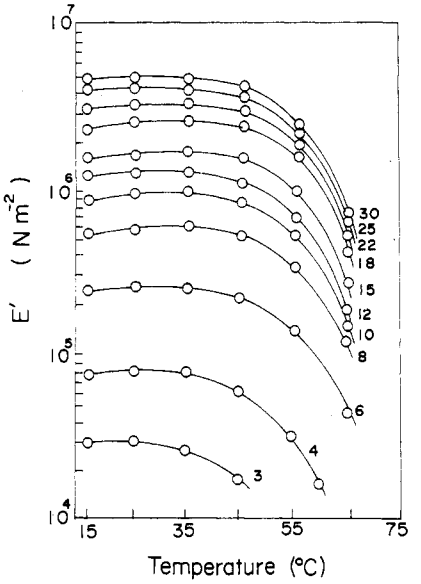


Figure 1. Temperature dependence of dynamic Young's modulus E' for agarose gels of various concentrations. The figures beside the curves represent the concentration percent (weight/weight).

extended chain length is given by Langevin function, so that the case of strong stretching of chains can be taken into account.[9] The both ends of each chain are bound to two of the junction zones by weak secondary interactions such as hydrogen bonds. The number of captured segments depends on temperature; i.e., the segments are released from the junction with increasing temperature and reeled in it with decreasing temperature. According to this model, the characteristic temperture dependence as shown in this figure may be explained in terms of bonding energy ϵ, the mean end-to-end distance r_m of chains which connect junction zones, and the ceiling number ν; i.e., the upper limit of the number of segments which can be liberated from junction zones just before the transition from gel to sol occurs. According to this treatment, the elastic modulus E increases monotonically for large values of bonding energy ϵ, mean end-to-end distance r_m, or the ceiling number ν, while E decreases monotonically for small values of these three parameters (Figure 2). Rubber is a typical example of the first family which shows the monotone increasing behavior; carrageenan and gelatin and many other thermoreversible gels belong to the second family which shows the monotone decreasing behavior. The temperature dependence of agarose gels shown in Figure 1 is a typical example of the third family, in which E increases up to a certain temperature and then decreases with increasing temperature. The mean end-to-end distance r_m may become shorter at higher concentrations in concentrated agarose gels through the formation of hydrogen bonds because there are many hydroxyl groups in agarose. Since the bonding energy does not seem to change with increasing concentration of gels as discussed later, the ceiling number ν must increase with increasing concentration of gels. Moreover, the increase in the ceiling number ν must be more important than the decrease of the mean end-to-end distance r_m.

The concentration dependence of the modulus is also of interest and may be discussed in the light of current theoretical models. The observed values of the Young's modulus at 25 °C, divided by three (Poisson's ratio assumed to be 0.5), are shown as a function of concentration (percent weight/weight) in Figure 3 (open circles). Calculated curves based on Clark and Ross-Murphy's cascade model[10] are also indicated (dotted, broken, dot-and-line, and solid lines). According to this approach the shear

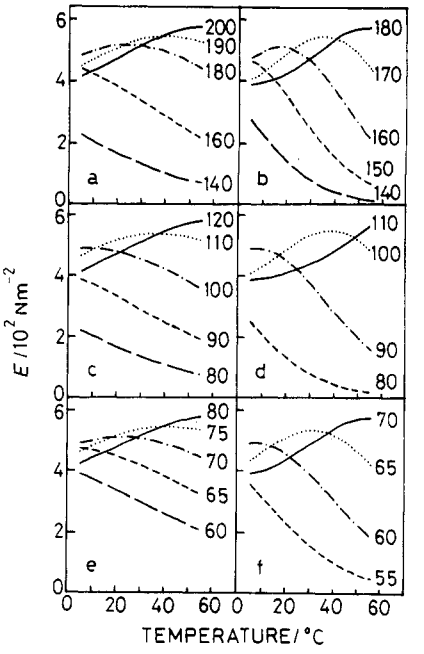


Figure 2. Temperature dependence of the elastic modulus calculated on the basis of a model consisting of junction zones which are connected by Langevin chains. The number of the chains in 1 cm³ is fixed as 10^{18}. The parameter $\mu = \nu/r_m$ is fixed as 2 for (a) and (b), 2.5 for (c) and (d), and 3 for (e) and (f). r_m is fixed as 100 times of a segment for (a), (c), and (e) and 400 times for (b), (d), and (f). The figures beside the curves represent the value of bonding energy ϵ (See the text).

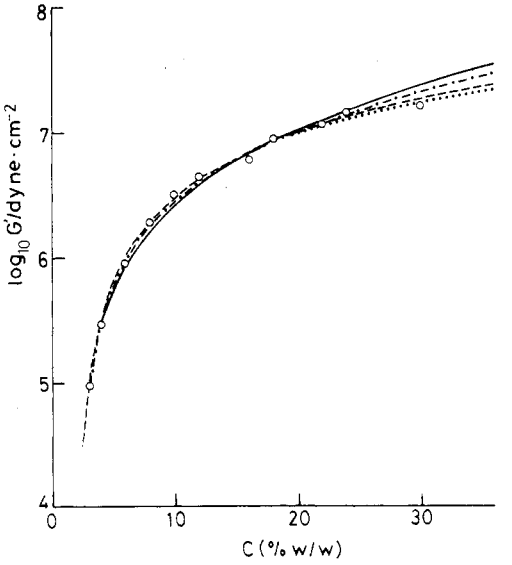


Figure 3. Concentration dependence of $G' = E'/3$ (open circles) of agarose gels at 25 °C. The curves are calculated for various values of f as a function of a reduced concentration C/C_0 by using the Clark and Ross-Murphy equation: (···) $f = 3$; (- - -) $f = 25$; (-·-) $f = 100$; (—) $f = 1000$.

modulus G is a function of three parameters f, K, and "a", where f is the functionality (number of sites per polymer molecule potentially available for bonding to others), K is an equilibrium constant for the cross-linking process (dm³/mol), and "a" is a nonideality factor measuring the extent to which the network deviates from ideal rubber behavior (i.e., aRT is assigned per mole of elastically active chains rather than RT). The equation describing the G versus C relationship is[10,11]

$$G = \frac{aRT(f-1)\alpha(1-v)^2(1-\beta)}{2000K(f-2)^2}\frac{C}{C_0} \quad (1)$$

Here α is the fraction of cross-linking sites which have reacted and is given by

$$\frac{\alpha}{Nf(1-\alpha)^2} = K \tag{2}$$

N being the number of polymer molecules per decimeter cubed ($=10C/M$) and M the molecular weight. The quantity v is the so-called extinction probability used in the cascade theory treatment[12] of network formation and is obtained as the lowest positive root of the equation

$$v = (1 - \alpha + \alpha v)^{f-1} \tag{3}$$

In addition in eq 1

$$\beta = (f-1)\alpha v/(1 - \alpha + \alpha v) \tag{4}$$

and C_0 is the critical concentration given by

$$C_0 = \frac{M(f-1)}{10Kf(f-2)^2} \tag{5}$$

Experimental G versus C data can easily be fitted by using eq 1 if f, a, and K are systematically varied until a best least-squares fit is achieved. In practice, however, since f is a poorly determined variable and is normally highly correlated with a and K, a better procedure is to fix f and do separate calculations in which a and K are optimized for each choice of f. The fits can then be compared.

In previous work of this kind using these methods Clark and Ross-Murphy[10] have fitted modulus–concentration data for gels from agar, gelatin, and a number of globular proteins. In general good fits were achieved, although the best of them corresponded to large values of the functionality f (i.e., $f \approx 100$). Particularly for the (heat-set) globular protein gels these values for f seemed implausibly high and the results were taken to indicate network imperfections not properly accounted for in the cascade treatment. For the agar gels, however, irrespective of f it was found that a was always greater than unity and this was taken to indicate the nonrubberlike nature of the elastically active chains present in agar gels.

In the present work, the elastic modulus (strictly Young's modulus) of the current agar systems was measured over a wide range of concentration, 11 data points being recorded in the interval C = 3–30% (w/w). These data were fitted by eq 1 and the procedures just described. In the calculations performed the agar molecular weight was set (rather arbitrarily) at 10^5 since no experimental value was available and this necessity, as will be discussed later, imposed some quite serious restrictions on the interpretation of results. In the fits attempted f, was set at various fixed values between 3 and 1000 and optimum values obtained for a and K in each case. The results are shown in Table I, which also lists corresponding estimates for C_0 obtained by applying eq 5. The indices of quality of fit are also shown in the table, and the nature of the fits achieved by the f = 3, 25, 100, and 1000 models are indicated by various broken and solid lines in Figure 3. It is clear that there is little difference in quality of fit for f less than 100, although a detailed study of the sum of squared residuals for the various analyses revealed that the best fit corresponded to the f = 25 model. In view of the highly aggregated nature of agarose gels indicated by much of the agarose gel literature and the current electron micrographs (Figure 10), the f = 25 result is physically quite reasonable. The double helix may be the primary cross-linking mechanism of the agar polymer when it forms aggregates, but in practice any one such molecule will engage in more than one such helical junction, and each junction is likely to be part of a substantial bundle of double-helical chain segments.

Table I
Optimized Values for a, C_0, and K Obtained by Least-Square Fitting Various Cascade Models (Equation 7) and Hermans Master Equation to the Agarose Data of Figure 3[a]

f	C_0, % (w/w)	K, dm^3/mol	a	$\sum\Delta^2$
3	1.71	0.3899×10^4	0.2899×10^3	0.01324
5	1.76	0.5061×10^3	0.1455×10^3	0.01679
10	1.73	0.8108×10^2	0.8765×10^2	0.01615
25	1.65	0.1101×10^2	0.5697×10^2	0.01294
50	1.58	0.2701×10	0.4527×10^2	0.01657
100	1.52	0.6803	0.3858×10^2	0.02531
1000	1.44	0.6968×10^{-2}	0.3173×10^2	0.04864

[a] $\sum\Delta^2$ is an indicator of the quality of fit being defined as $=\sum(\log G_i^{\text{obsd}} - \log G_i^{\text{calcd}})^2$.

Finally, though examination of the values of a and K which emerge, particularly for the f = 25 model, should in principle reveal extra information about the agar network such as the degree of nonideality of the network strands (in relation to ideal rubber models) and the strength of the cross-links formed, this is frustrated in the present case by the lack of an experimental molecular weight (weight average, for example). The value assumed in calculations (10^5) may well be too high, judging by the unusually high critical concentration of the present agar, and any such discrepancy will directly influence a and K (halving M for example halves a and K).

However, even if M was overestimated by as much as a factor of 10, the lowest value of a which would emerge from calculations would be ~3 and this is still greater than the rubber theory prediction of unity. As has been concluded elsewhere,[10] the elastically active chains in agar gels are much stiffer than those envisaged by the theory of rubber elasticity (i.e., they are enthalpic rather than entropic), a result which is quite in accordance with the structure of such strands if they are envisaged as composed of bundles of agar helices separated by short segments of a sterically hindered polysaccharide coil.

Before leaving the topic of the concentration dependence of the agar gel modulus, it is worth noting that at least one other model has been published which provides a quantitative description of the G versus C relationship. This is the model described by Oakenfull.[13] This model envisages the cooperative formation of "junction zones" through the clustering together of chain segments (single or double helices), an equilibrium constant again controlling the extent of the process. In a later publication we shall compare and contrast this approach with the current one in relation to its ability to describe modulus concentration data for systems of the agar gel type.

Gel–Sol Transition by Differential Scanning Calorimetry. Figure 4 shows the heating DSC curves for agarose gels of various concentrations. An endothermic peak accompanying the gel–sol transition appeared at about 75 °C, and it shifted slightly to higher temperatures with increasing concentration of agarose gels. Although the Eldridge-Ferry plot was originally proposed for dilute gels, we have already made the plot of concentration against the inverse of the melting temperature for concentrated agarose gels and found this relation to be a straight line up to 18% (w/w).[5] The enthalpy, ΔH_m, of formation of network junctions estimated from the slope of this straight line was 1.5–1.6 $\times 10^3$ kJ/mol. The reason why this plot is a straight line even up to 18% is not clear at present. However, the Eldridge-Ferry plot for the present very concentrated agarose gels was not a straight line but showed convex curvature. An exothermic peak appeared at about 30 °C, and it also shifted slightly to

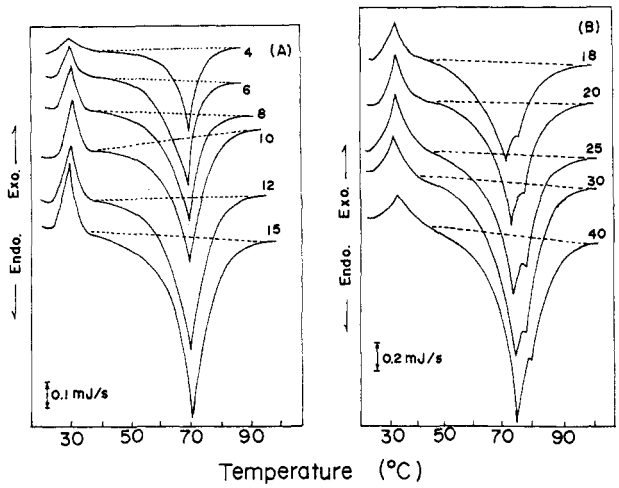


Figure 4. Heating DSC curves for agarose gels of various concentrations. The figures beside the curves represent the concentration in percent (weight/weight): (A) previous results;[5] (B) present work.

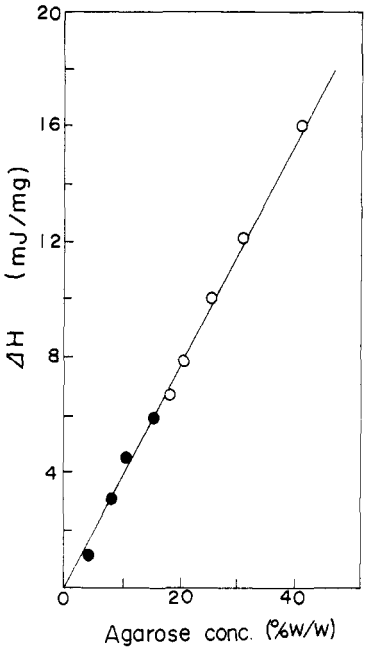


Figure 5. Relation between the endothermic enthalpy and the concentration of agarose: (●) previous results;[5] (○) present work.

higher temperatures with increasing concentration of gels. This exothermic peak has been attributed to the increase of ordered regions through the rearrangement of molecular chains during heating just before the dissolution of the gel, and this is mainly induced by syneresis. This exothermic peak became a maximum at about 25%, at which concentration the gel must be most crystalline. This peak was not observed in carrageenan or gelatin gels.

The relation between the endothermic enthalpy and the concentration of agarose gels is shown in Figure 5 together with previous results.[5] The endothermic enthalpies were evaluated from the areas surrounded by the endothermic peaks and base lines shown in Figure 4. The endothermic enthalpy was proportional to the concentration of agarose gels over a wide concentration range. Since the number of cross-linking points is proportional to the concentration, the bonding energy ϵ, proportional to the endothermic enthalpy ΔH divided by the concentration, is independent of the concentration even at very high concentrations.

Figure 6 shows the heating DSC curves of a 25% (w/w) agarose gel at different heating rates. The reason why the endothermic curve accompanying gel–sol transition showed

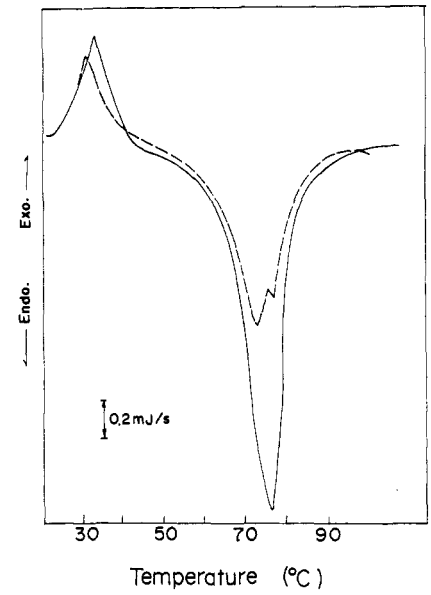


Figure 6. Heating DSC curves of a 25% (w/w) agarose gel at different heating rates. Heating rate: 2 °C/min (---); 4 °C/min (—).

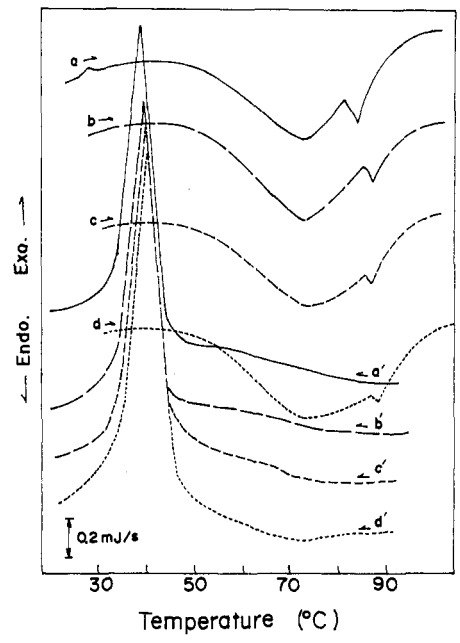


Figure 7. DSC curves of concentrated agarose gels. Heating and cooling rate, 2 °C/min: (a) reheating, (a') cooling for a 25% (w/w) gel; (b) reheating, (b') cooling for a 30% (w/w) gel; (c) reheating, (c') cooling for a 35% (w/w) gel; (d) reheating, (d') cooling for a 40% (w/w) gel.

two peaks may be attributed to the polymorphism in concentrated gels because these two peaks became only one peak when the heating rate was increased from 2 to 4 °C/min.[14] Multiple endothermic peaks in DSC are observed in the melting of polymeric crystals with different lattice defects or different morphologies. They are also observed in the polymeric crystal melting which accompanies a crystal transition, or recrystallization, or a chemical reaction. In our concentrated agarose gels, the double endothermic peaks seemed to be induced by the formation of deformed crystals as was observed in κ-carrageenan gels.[15]

Figure 7 shows heating and cooling DSC curves of agarose gels of various concentrations. In order to clarify the origin of a small exothermic peak at about 30 °C, the following points were examined. The sample gel sealed

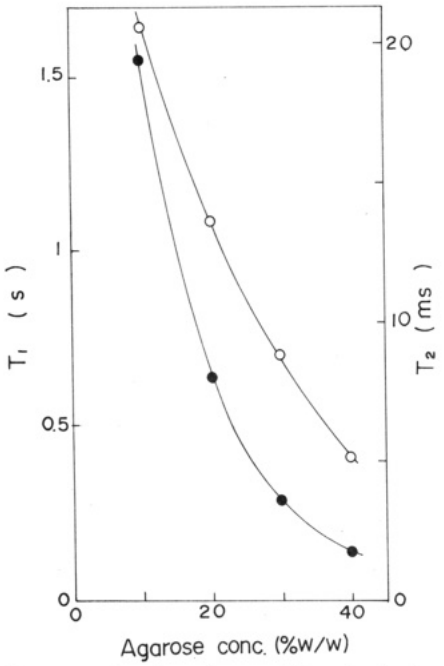


Figure 8. Concentration dependence of the spin–lattice relaxation time T_1 (○) and the spin–spin relaxation time T_2 (●) of agarose gels.

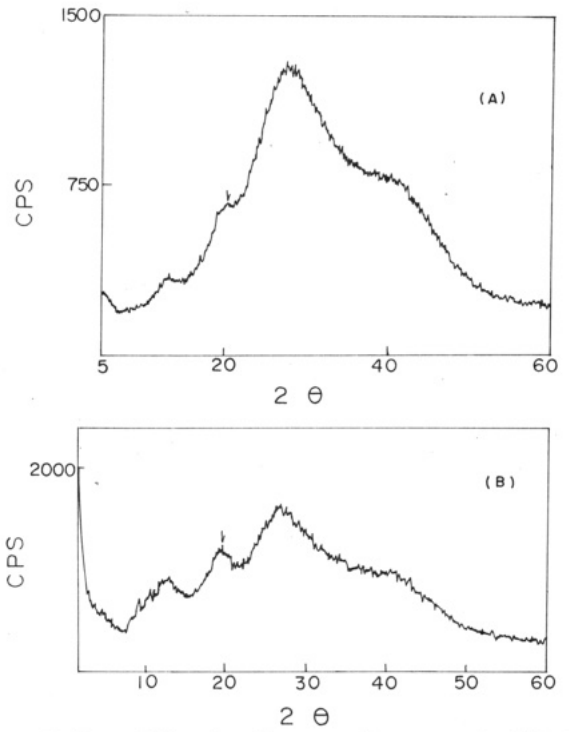
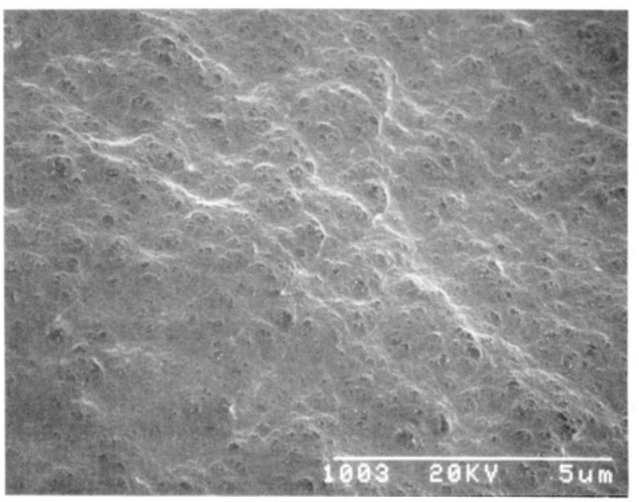


Figure 9. X-ray diffraction diagrams of agarose gels: (A) 15% (w/w); (B) 30% (w/w).

in a DSC cell was heated to 100 °C at the rate of 2 °C/min, kept at 100 °C for 10 min, cooled to 5 °C at a rate of 2 °C/min, and then maintained at 5 °C overnight before the DSC measurement was carried out. Then the heating DSC curves were observed at a heating rate of 2 °C/min. These reheating DSC curves (a–d) not only did not show a small exothermic peak at about 30 °C, but in addition to this, the endothermic peak accompanying the gel dissolution became broader in comparison to the first-run heating DSC curves shown in Figure 3. After keeping the temperature at 100 °C for 10 min, the cooling DSC curves (curves a′–d′) were observed at a cooling rate of 2 °C/min. A sharp exothermic peak accompanying gel formation was observed. The transition temperatures of agarose gels for the gel formation and the gel dissolution were different. The temperature of the gel dissolution shifted slightly to higher temperatures with increasing concentration, and the temperature of the gel formaton shifted also to higher temperatures with increasing concentration. The shift for the latter is more remarkable than that for the former. The difference ΔT between the temperatures for the gel formation and for the gel dissolution became smaller with increasing concentration. The difference ΔT became more pronounced when the rate of heating and cooling increased, although the data are not shown here. A small exothermic peak in the first-run heating DSC curves shown in Figure 3 was attributed to the formation of ordered regions promoted by syneresis during heating as reported previously.[5] When the sample is once heated to 100 °C and is dissolved, the gel formed by cooling adheres to the inner surface of a DSC cell. Then the free surface of the gel decreases in comparison to that in the first-run heating. Therefore, the volume change and also the syneresis during heating are suppressed, and a small exothermic peak which appears in the first-run heating disappears in the reheating DSC curves.

State of Water in Agarose Gels. Figure 8 shows the concentration dependence of the spin–lattice relaxation time T_1 and the spin–spin relaxation time T_2. Over the observed temperature range, bound water protons are expected to relax faster than the free water protons. Since



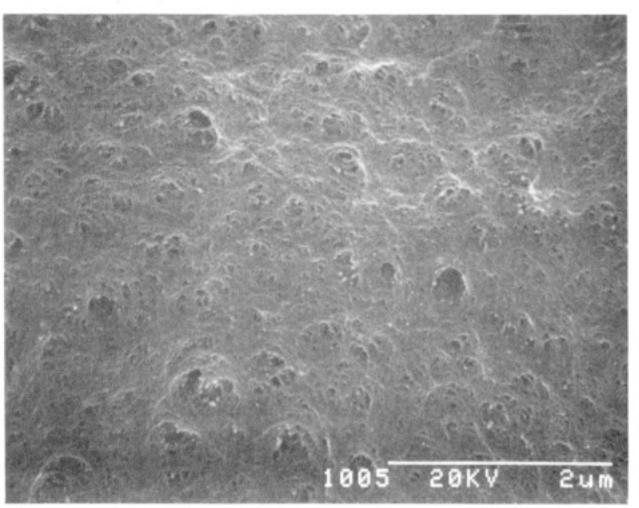


Figure 10. Scanning electron micrographs of 30% (w/w) agarose gels (×7400 and ×14800).

the movement of bound water protons is restricted, it must be less effective in averaging the dipolar interactions. The relaxation time decreased with increasing concentration of agarose gels. This is quite consistent because bound water content increases with increasing concentration of agarose gels as shown in DSC analysis. The fact that the observed relaxation time is unique, although the movements of protons in bound water and free water are different, may be understood in terms of the rapid exchange model proposed by Zimmerman and Brittin,[16] as was discussed by Ablett et al. in the case of agarose gel[17] and by Maquet et al. in the case of gelatin gels.[18]

Structure of Agarose Gels. X-ray diffraction diagrams of 15% and 30% agarose gels are shown in Figure 9. Only a halo, characteristic of amorphous materials, was observed in X-ray diffraction patterns from gels whose concentration was less than 25%, but beyond this concentration a sharp peak characteristic of crystalline materials was observed at 20°. These peaks became more prominent with increasing concentration of gels. Note that the scales of the ordinates of parts A and B of Figure 9 are different. The helical chain segments are forced to aggregate to make a bundle and give rise to junction zones. This process is promoted by the increase of concentration of polymers. This situation is similar to the formation of liquid crystals of, e.g., poly(γ-benzyl L-glutamate); the rigid-rod molecules are obliged to orientate at higher concentrations.

Figure 10 shows the scanning electron micrographs of a 30% agarose gel. Dense networks are observed in these photographs and these, are quite different from the porous structures observed in dilute gels, although they are not shown here. The densely packed regions are thought to be junction zones which consist of a bundle of double-helical chain segments.

Registry No. Agarose, 9012-36-6.

References and Notes

(1) Rees, D. A. *Pure Appl. Chem.* **1981**, *53*, 1.
(2) Indovina, P. L.; Tettamanti, E.; Micciancio-Giammarinaro, M. S.; Palma, M. U. *J. Chem. Phys.* **1979**, *70*, 2841.
(3) Tokita, M.; Hikichi, K. *Phys. Rev. A* **1987**, *35*, 4329.
(4) Hayashi, A.; Kanzaki, T. *Food Hydrocolloids* **1987**, *1*, 317.
(5) Watase, W.; Nishinari, K. *Makromol. Chem.* **1987**, *188*, 1177.
(6) Watase, M.; Nishinari, K. *Rheol. Acta* **1983**, *22*, 580.
(7) Watase, M.; Nishinari, K. *Nippon Shokuhin Kogyo Gakkaishi* **1983**, *30*, 368.
(8) Nishinari, K.; Koide, S.; Ogino, K. *J. Phys. (Paris)* **1985**, *46*, 793.
(9) Treloar, L. R. G. *The Physics of Rubber Elasticity*; Clarendon Press: Oxford, 1975.
(10) Clark, A. H.; Ross-Murphy, S. B. *Br. Polym. J.* **1985**, *17*, 164.
(11) Clark, A. H. In *Food Structure and Behaviour*; Blanshard, J. M. V., Lillford, P. J., Eds.; Academic Press: New York, 1987; Vol. 1, pp 13–34.
(12) Gordon, M.; Ross-Murphy, S. B. *Pure Appl. Chem.* **1975**, *43*, 1.
(13) Oakenfull, D. *J. Food Sci.* **1984**, *49*, 1103.
(14) Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1980; Vol. 3, Crystal Melting.
(15) Watase, M.; Nishinari, K. In *Gums and Stabilisers for the Food Industry* 3; Phillips, G. O., Wedlock, D. J., Williams, P. A., Eds.; Elsevier Applied Science Publishers: London, 1985; pp 185–194.
(16) Zimmerman, J. R.; Brittin, W. E. *J. Phys. Chem.* **1957**, *61*, 1328.
(17) Ablett, S.; Lillford, P. J.; Baghdadi, S. M. A.; Derbyshire, W. *J. Colloid Interface Sci.* **1978**, *67*, 355.
(18) Maquet, J.; Théveneau, H.; Djabourov, M.; Lebrond, J.; Papon, P. *Polymer* **1986**, *27*, 1103.

Electron Spectroscopy for Chemical Analysis Study of the Surface Oxidation of Poly(phenylene sulfide) Powder by Heterogeneous Reactions†

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ABSTRACT: The oxidation of poly(phenylene sulfide) (PPS) powder investigated by electron spectroscopy for chemical analysis (ESCA), in terms of the extent of reaction, suggests that a random terpolymer type of a surface layer is generated consisting of sulfide, sulfoxide, and sulfone groups. Slurry conditions, in two reaction schemes, were employed since a good solvent is not available for PPS. It was expected that the surface of the polymer particle would be oxidized. Reaction A was carried out at 60 °C in toluene with a mixture of formic acid and hydrogen peroxide as the oxidizing agent while reaction B was carried out in a methylene chloride medium at 25 °C with 3-chloroperoxybenzoic acid. ESCA results indicate that up to 75% of the sulfide (—S—) sulfur is oxidized to sulfoxide (—[S=O]—) and sulfone (—[O=S=O]—) in the surface region. The phenyl ring is unaffected. Depth profiling with Ar^+ ion sputtering (~100 Å) indicates that the reactions have also occurred in the subsurface region, but to a lesser extent.

Introduction

The primary objective of this study is to evaluate the extent and nature of the oxidation of poly(phenylene sulfide) (PPS) by a wet chemical process. Since the polymer does not have a good solvent, the reaction was carried out under slurry conditions.

The heterogeneous reactions have been found to generate sulfoxide and sulfonyl groups on the surface by the oxidation of the sulfide group. The resulting polymer powder is studied by electron spectroscopy for chemical analysis (ESCA) in order to gain insights into surface-enhanced slurry reactions. For example, Clark and Stephenson[1] used ESCA to study the nitration of cellulose fibers. Zadorecki and Ronnhult[2] have also used this technique to characterize cellulose fibers in the form of paper sheets chemically modified with trichloro-*s*-triazine. Millard[3] has studied corona-treated wool fibers while Carr et al.[4,5] have characterized chemically treated wool fibers by ESCA.

The crystal structure of PPS has been determined by Tabor et al.[6] by X-ray diffraction and IR. The electronic structure has been studied by Riga et al.[7] using ESCA.

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