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Melting temperatures of thermally reversible gels

IV. Methyl cellulose-water gels

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With 5 figures and 4 tables

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Introduction

Dilute solutions of methyl cellulose (abbreviated MC) in water set to a gel on warming. On cooling the gel, it reverts to the sol state. The sol-gel transition may be made reversible on cycling the temperature, and the temperature dependence of this sol-gel transition cycles is just opposite when compared with other thermally reversible gels (e.g. gelatin in water and agar in water). This thermally reversible sol-gel transition was first investigated by *Heymann* (1) and he attributed the gelation to the dehydration of hydrated MC molecules by raising the temperature. It is well known that reversible crosslinks must exist in any reversible gel. Hydrogen bonds, hydrophobic bonds and dipolar interactions between polymer chains may be candidates of the reversible crosslinks. Fringed micelle type crystallites may also serve as the crosslinks. For any thermally reversible gel, it is primary importance to clarify the nature and structure of crosslinks.

Efforts have been devoted to this end. *Kuhn, Moser and Majer* (2) concluded that the aggregation of MC molecules held together by dipolar force leads to gelation. On the other hand, *Rees* (3) has suggested that a sort of liquid-liquid phase separation, namely a micelle formation, is responsible for gelation of methyl cellulose solution. It has been reported (4) that MC polymer prepared by heterogeneous reaction converts to gel whereas the homogeneously substituted MC does not. The MC prepared by the former method is an alternative block copolymer which consists of densely substituted hydrophobic and less substituted hydrophilic block sequences. The

hydrophobic parts are considered to form a structure of water around them, and on raising the temperature, these water structures are disrupted. The densely substituted parts of MC form droplets, while the hydrophilic parts prefer to remain in water preventing coalescence of the droplets. Therefore, the droplets are actually described as micelles and act as "cross linking loci". This is of course a sort of liquid-liquid phase separations. Although this suggestion is a very attractive explanation for the mechanism of gelation of MC, it has not been evident, however, that whether the onset of gelation corresponds to thermodynamic conditions consistent with a liquid-liquid or a crystal-liquid transition. Therefore, inspite of these studies, the nature and structure of "cross linking loci" of thermally reversible MC gel are not still clear.

Since the copolymeric character is conducive to gel formation, on assuming crystalline crosslinks and then introducing the free energy of crystallization for the copolymer-diluent systems into the probability requirement of gel points (5), we have derived the following equation (6)

$$\frac{1}{T_m^g} = \frac{\zeta}{\left(\zeta \Delta b_u + \left(\frac{V_A}{V_1} \right) \psi_1 \Theta R \zeta - 2\sigma_{ec} \right)} \cdot \left(\frac{\Delta b_u}{T_m^o} + \frac{R V_A}{V_1} \left(\frac{1}{2} + \psi_1 \right) - R \ln X_A \right) - \frac{R}{\left(\zeta \Delta b_u + \left(\frac{V_A}{V_1} \right) \psi_1 \Theta R \zeta - 2\sigma_{ec} \right)} \cdot \ln v_{2x} \quad [1]$$

where, T_m^g is the melting temperature of gel, T_m^0 the equilibrium melting temperature, ν_2 the volume fraction of the copolymer in the gel, \times the number of the repeating unit (\overline{DP}), ζ is the number of the crystallized unit which has entered into the crystallite as a sequence, X_A the mole fraction of crystallizable unit, Δh_u the heat of fusion per repeating unit, σ_{ec} the end interfacial free energy per crystalline sequence, ψ_1 the entropy of dilution parameter, Θ theta temperature, and V_A and V_1 are molar volumes of the unit and solvent, respectively.

It is quite important to notice that the gel melting temperature (T_m^g) is not a thermodynamic singularity as pointed out previously (6). From the *Eldridge-Ferry* (7) type plot, i.e., $1/T_m^g$ vs. $\ln \nu_2 \times$ plot, the equation allows us to estimate both the crystalline sequence length ζ and the interfacial free energy σ_{ec} .

The method has been successfully applied to various thermally reversible gel systems (6) in order to estimate both ζ and σ_{ec} . Moreover, for the poly(vinyl chloride)-dioxane gel, *Haas* (8) has shown that the value of ζ estimated from the above method is adequately compared with ζ values which were estimated from both swelling and elastic properties of the gel.

In this report, we first examine the structure of "cross linking loci" by X-ray method. And if they appear as crystallites, then on applying the above equation we may estimate the crystalline sequence length ζ from the gel melting temperatures. To this end, both the dilute solution properties of MC and the melting point depression of MC-diluent systems are also studied in order to estimate ψ_1 , Θ and Δh_u .

Experimental

Materials

Ten samples of methyl cellulose which differ in molecular weight have been used. All the polymers were purified by dissolving them in cold water, precipitating the solution in an aceton-water mixture, and washing the precipitate by methanol and benzene, and they were dried *in vacuo* for three days at 100 °C.

Degree of substitution (DS) or methoxyl content of the polymers were determined by the method used by *Samsel* and *McHard* (9) or by pycnometer (10).

Characterization of Polymers; Molecular weight of MC samples were determined by viscosity measurements in water at 20 °C using the following viscosity equation (11),

$$[\eta] = 2.8 \times 10^{-3} M^{0.63} \quad [2]$$

where $[\eta]$ means the intrinsic viscosity and M the molecular weight.

Table 1. Characteristics of Methyl Cellulose

Samples	DS	$[\eta]$ in water 20 °C	$\overline{M}/10^4$	$\overline{DP} (= \times)$
MC-1	1.21	2.6	5.1	290
MC-2	2.09	4.5	12.3	640
MC-3	1.39	6.1	19.9	1100
MC-4	1.52	7.2	26.2	1430
MC-5	1.62	7.7	28.8	1560
MC-6	1.84	7.8	29.4	1570
MC-7	1.29	11.6	55.2	3060
MC-8	1.81	17.9	109.8	5860
MC-9	1.68	9.3	39.0	2100
MC-10	1.76	6.6	22.5	1210

Molecular characteristics of the samples are given in table 1.

Thermodynamic Properties; The thermodynamic properties of MC-water solutions were determined by osmometry using a Mechrolab High Speed Membrane Osmometer Model 502 fitted with a regenerated cellulose membrane.

Heat of fusion of MC was estimated from the melting point depression of MC-diluent systems. Ethylene glycol, diethylene glycol and propylene glycol were used as diluents. Values of melting point of MC-diluent systems were obtained by observing the samples between crossed nicols with polarized light and noting the disappearance of depolarization upon melting or by visual inspection of the disappearance of turbidity of the mixture on stirring. It was found that the both methods give almost identical melting points.

Melting Temperature and X-ray Diffraction of Gels; Gels of MC were prepared at 60 °C for 4 hr in U-shaped tubes as described previously for poly(vinyl chloride) gels (6). The U-tubes were then cooled at the rate 1 °C/5 min and the temperature at which a pressure head caused flow through a fine capillary was used as the melting temperature of gel (T_m^g).

The X-ray diffractograms of a cellulose filter paper, MC films and the MC gel were obtained by a Rigaku Geigerflex SG-7. For the MC gel, a special cell holder was used for maintaining the temperature of gel at 50 °C. The cell holder was blanketed by saturated water vapor in order to avoid the drying of gel.

Results

Despite the samples in their methoxyl content ranging from 1.2 to 2.09, they were all converted to gels by simply raising temperature. It was observed that a considerable turbidity appeared in the gel state and this disappeared in the sol state. In figure 1, the reciprocals of the gel melting temperature are plotted against $\ln \nu_2 \times$ for three MC gels. The plots are linear

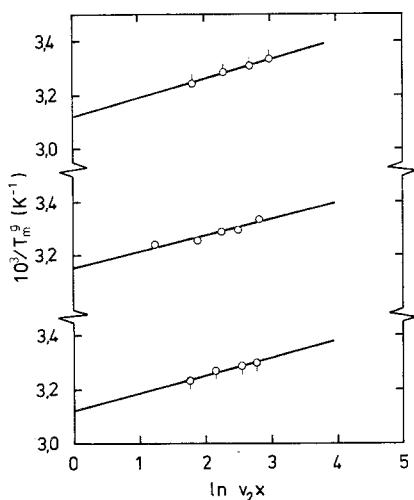


Fig. 1. Examples of the reciprocal of the gel melting temperature vs. $\ln v_2^x$ plots for methyl cellulose samples. \circ , for MC-4; \bigcirc , for MC-6; φ , for MC-9

indicating that the Eldridge-Ferry-like plot is still applicable to this inverted gelling systems with positive slopes. For the other MC gels, straight lines were also obtained. The intercepts and the slopes determined from these plots are summarized in table 2.

In order to analyse the results according to equation [1], we first need the proof that the "cross linking loci" are crystallites or crystalline nuclei, since in the derivation of equation [1] it was assumed that the "crosslinks" are crystallites.

Comparisons of three X-ray diffractograms of the cellulose filter paper, the dried MC film cast from its aqueous solution, and the MC gel are made in figure 2. In table 3, the observed d -spacings are summarized. The X-ray diffrac-

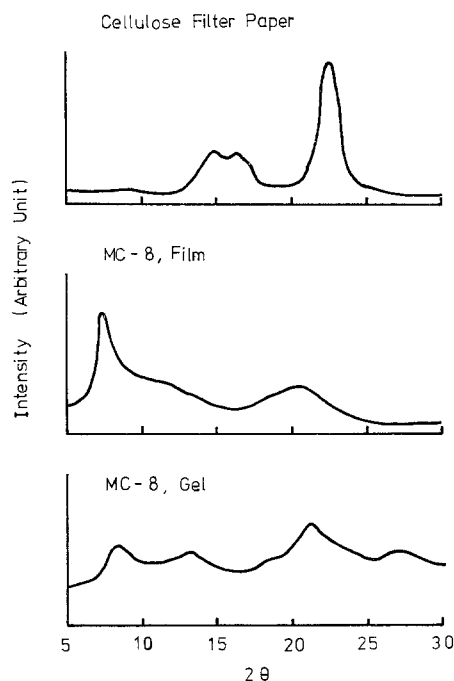


Fig. 2. Comparison of X-ray diffractograms of cellulose filter paper, of the dried MC film and of the MC gel. MC-8 is used as a sample

tograms of both the MC film and the gel are clearly different from that of cellulose, and moreover, the diffractograms of the MC-film and the gel give diffraction peaks which locate almost the same 2θ , except the peaks of

Table 2. Experimental results

Samples	Intercept $\times 10^3 \text{ K}^{-1}$	Slope $\times 10^5 \text{ K}^{-1}$	ζ	$\sigma_{ec}/10^3$ (J/mol)
MC-1	3.10	7.50	4.4	-28.8
MC-2	3.18	4.80	6.7	-42.2
MC-3	3.09	8.00	4.2	-28.4
MC-4	3.12	7.17	4.6	-30.1
MC-5	3.10	7.15	4.6	-30.1
MC-6	3.15	6.15	5.3	-34.3
MC-7	3.08	7.25	4.5	-28.8
MC-8	3.16	4.30	7.6	-48.9
MC-9	3.12	6.32	5.2	-33.9
MC-10	3.15	6.50	5.1	-33.9

Table 3. Results of X-ray diffraction measurement

Samples	2θ	d (nm)	Intensity*	Index
Cellulose filter paper				
	14.5	0.611	<i>m</i>	101
	16.1	0.550	<i>m</i>	10 $\bar{1}$
	22.4 ₈	0.395	<i>vs</i>	002
	34	0.264	<i>vw</i>	301
Methyl cellulose film				
MC-4	8.4	1.05	<i>vs</i>	—
($DS=1.52$)	20.9 ₄	0.515	<i>vs</i>	—
MC-8	7.63	1.16	<i>vs</i>	—
($DS=1.81$)	20.2	0.440	<i>s</i>	—
Methyl cellulose gel				
MC-8	8.1	1.09	<i>m</i>	—
$C=10 \text{ wt } \%$	13.2	0.671	<i>m</i>	—
	21.08	0.421	<i>s</i>	—
	26.88	0.33 ₂	<i>w</i>	—

* *vs*, very strong; *s*, strong; *m*, middle; *w*, weak; *vw*, very weak.

$2\theta = 13.2$ and 26.88 for the gel. The $2\theta = 13.2$ and 26.88 peaks are due to water (12). Furthermore, those peaks of $2\theta \approx 7.63$, $2\theta \approx 20$ for the MC-film, and $2\theta = 8.1$, $2\theta = 21$ for the gel, respectively, well coincide with the peak positions of trimethyl cellulose reported by *Trogus and Hess* (13), and *Mark and Susich* (14). It is concluded that the "cross linking loci" MC gels consist of the crystallites of trimethyl glucose sequences.

Therefore, it may also be expected that the heat of fusion of MC may be determined if suitable diluents are found. Ethylene glycol, diethylene glycol and propylene glycol were found as such diluents. In copolymer diluent systems, both the copolymer composition and the polymer concentration affect the melting point. According to *Flory* (15), the melting point of a copolymer-diluent system is given by

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta b_u} \left\{ \left(\frac{V_A}{V_1} \right) v_1 - \chi_1(1 - v_A)^2 - \ln X_A \right\} \quad [3]$$

where T_m^0 is the melting point of pure trimethyl cellulose, T_m the melting point of a MC containing mole fraction X_A of crystallizable trimethyl glucose units with volume fraction v_1 of diluent. Δb_u the enthalpy of fusion of trimethyl glucose unit, V_A and V_1 are the molar volumes of the unit and diluent, respectively. v_A is the volume fraction of trimethyl glucose unit, while χ_1 is the interaction parameter between the trimethyl glucose unit and the "solvent medium" which consists of diluent and the noncrystallizable comonomer. When polymer concentration is very low, equation [3] may be approximated as

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta b_u} \left\{ \left(\frac{V_A}{V_1} \right) (1 - \chi_1) - \ln X_A \right\} \quad [4]$$

For a specified diluent, neglecting the temperature dependence of χ_1 , equation [3] predicts a linear relationship between $1/T_m$ and $\ln X_A$. The data obtained at three concentrations in ethylene glycol are plotted in figure 3. In figure 4 the plots between $1/T_m$ and $\ln X_A$ are shown for three diluents at the same concentration. Taking the best straight line, we

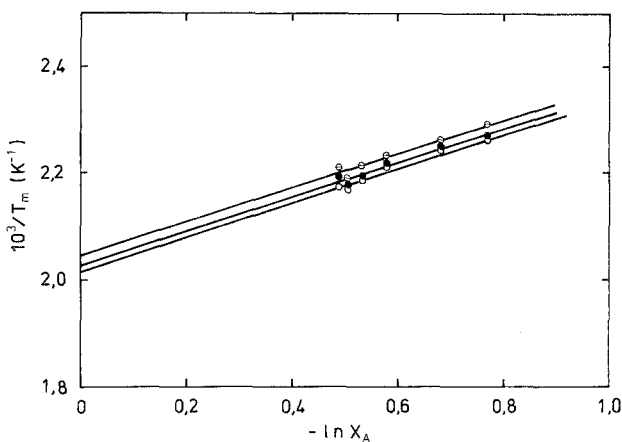


Fig. 3. Plots of the reciprocal of the melting temperature vs. $\ln X_A$ in ethylene glycol as diluent: \ominus , 5 wt%; \bullet , 8 wt%; \circ , 11 wt%

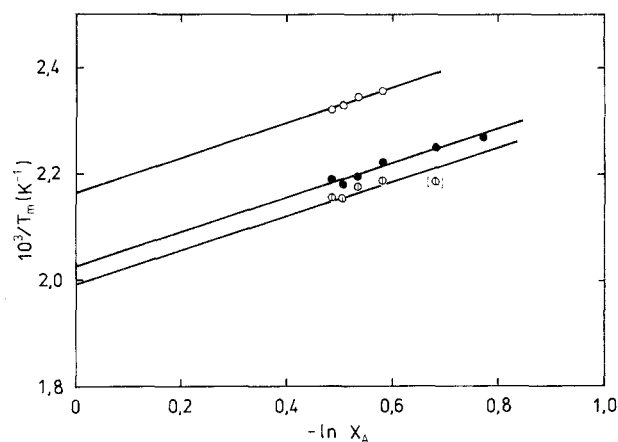


Fig. 4. Plots of $1/T_m$ vs. $\ln X_A$ in three different diluents at polymer concentration 8 wt%. \circ , in propylene glycol; \bullet , in ethylene glycol; \odot , in diethylene glycol

obtain $\Delta b_u = (2.6 \pm 0.4) \times 10^3$ J/mol. *Haworth* (16) reported that the melting point of trimethyl cellulose (T_m^0) is 488 K. The entropy of fusion $\Delta S_u = 5.0$ J/mol·deg is evaluated from the above figures. Low values of Δb_u are commonly obtained from the application of the theory of melting point of copolymers (17). However, the value of ΔS_u is almost identical with the value of ΔS_u of cellulose nitrate (18).

The entropy parameter ψ_1 and the theta temperature of MC-water solution were evaluated from the temperature dependence of the observed osmotic second virial coefficient. Osmotic pressure measurements of higher molecular weight MC samples were examined,

however, it was observed that the attainment of equilibrium osmotic pressure was quite slow and moreover the observed molecular weights increased with the increase of temperature indicating aggregation. Only successful data were obtained for the lowest molecular weight sample MC-1, and the results are shown in figure 5. According to the plot of A_2 vs $1/T$, the Θ temperature is 320 K.

The dilute polymer solution theory (19) gives

$$A_2 = (\bar{v}^2/V_1) \left(1 - \frac{\Theta}{T}\right) \psi_1 b(z) \quad [5]$$

where \bar{v} and V_1 are the partial specific volume of polymer and the molar volume of solvent, respectively, and $b(z)$ is a function whose value is unity at $T = \Theta$. If we neglect the variation of $b(z)$ with temperature, then we can estimate $\psi_1 = -1.67$ for the entropy parameter from the temperature coefficient of A_2 in the vicinity of $A_2 = 0$.

Making use of $\Delta h_u = 2.6 \times 10^3$ J/mol, $T_m^0 = 488$ K, $\psi_1 = -1.67$ and $\Theta = 320$ K, the crystalline sequence length ζ of trimethyl glucose units and the end interfacial free energy σ_{ec} are estimated from the observed intercepts and slopes. The procedure to obtain ζ and σ_{ec} has been predicted previously (6). The results are shown in table 2 and the values of ζ are in the range of 4 ~ 8.

Discussion

The X-ray diffractogram of the MC gel showed unambiguously the presence of crystal-

line order in the gel. The values of ζ indicate that small runs of trimethyl glucose sequences in MC chains are responsible for the order.

Usually methyl cellulose is prepared by the heterogeneous reaction, that is, the reaction between alkali cellulose and methylene chloride. Timell (20) has investigated the fractions of mono-, di- and tri-methyl glucose units in MC chains prepared by the heterogeneous reaction. The fraction of trimethyl glucose unit (S) increases with the degree of substitution (DS). Spurlin (21) reported that S is equal to $(DS/3)^3$. The average number (Ω) of trimethyl glucose sequences of size ζ per MC chain is given by

$$\Omega = x\zeta(1 - S)S^{\zeta-1} \quad [6]$$

where x is the degree of polymerization (15). Since at the gel point each polymer chain goes through at least two crystallites, Ω is equal to 2 (19, 22). The critical sequence length ζ_c which is capable of crystallizing to form the three dimensional MC network in water may be easily estimated by putting $\Omega = 2$ for given x and S . The calculated ζ_c is compared with the observed ζ in table 4. It is obvious that the critical crystalline sequence length ζ_c almost coincides with the observed ζ . The fact also supports that the "cross linking loci" are the crystallites which consist of trimethyl glucose units.

The other support of the presence of crystalline order in the gel stems from the following observation. The effects of both gelation temperature and gelation time were examined. It was observed that the higher the gelation temperature, the lower the gel melting point. The longer gelation time

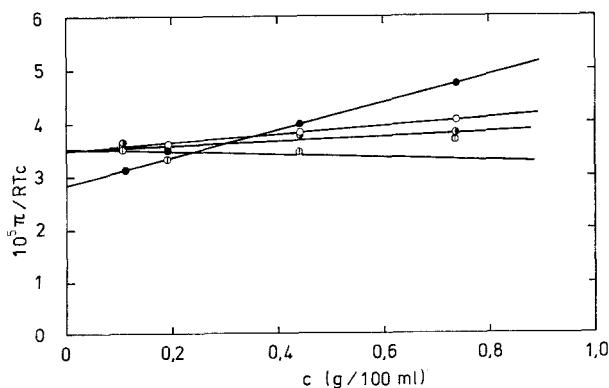


Fig. 5. Results of osmotic pressure measurement for MC-1 at various temperatures: ●, 30 °C; ○, 40 °C; ●, 45 °C; ○, 50 °C

Table 4. Comparison between observed ζ and calculated ζ_c with equation [6]

Samples	x	s	ζ_c	ζ
MC-1	290	0.066	3.2	4.4
MC-2	640	0.338	7.3	6.7
MC-3	1100	0.099	4.4	4.2
MC-4	1430	0.130	4.9	4.6
MC-5	1560	0.155	5.4	4.6
MC-6	1570	0.231	6.6	5.3
MC-7	3060	0.080	4.4	4.5
MC-8	5860	0.220	7.4	7.6
MC-9	2100	0.176	5.9	5.2
MC-10	1210	0.202	6.0	5.1

produced quite the same effect. *Frenkel* (23) discussed the thermokinetics of formation of crystalline nuclei and ordered structures in polymer solutions and gels, and the present observation is in accord with his concept.

It may be inclined that both the negative entropy and enthalpy of dilution parameter as well as $\Theta = 320$ K support the idea that "hydrophobic bonding" should be responsible for the gelation of MC-water system through formation of "cross linking loci" of liquid like micelles. However, for most water soluble polymers, the liquid-liquid type phase separation by raising the temperature is rather a rule. It is quite important to notice that the theta temperature (47 °C) is very close to the gelation temperature of MC in water. The reported gel points are 40 °C for 10% MC and 50 °C for 5% MC, respectively (24). This fact may explain why controversial conclusions have been reached for the mechanism of gelation of MC in water. As *Mandelkern* has pointed out first (17) and as also the present analysis shows, the inverted gelation is the consequence of the magnitude and sign of the free energy of dilution $[(V_A/V_1)\psi_1\Theta R\zeta]$ relative to that of fusion ($\zeta\Delta h_u$).

A liquid to crystal phase transition is occurring in this case. Phase separations similar to this MC-water system are exhibited by cellulose nitrate in dilute ethanol solution (25) as well as poly(L-proline) in water (26). The temperature dependence of gel melting temperature of MC is the manifestation of the crystallization.

The interfacial free energy σ_{ec} was negative and, on the average, -33.9×10^3 J/mol or -8100 cal/mol of crystalline sequence. The high and negative value that characterize σ_{ec} must be related to the molecular nature of the interface of crystallite. This interface, of course, involved the passage of a connected sequence of chain units from the crystallite to the aqueous phase. On passing from the region of crystalline order to that of disordered aqueous phase, the nature of units of a given MC chain changes from hydrophobic to hydrophilic. Moreover, this change cannot occur over the interval of one unit.

The less substituted hydrophilic units may be stabilized by hydrogen bonds between hydroxyl groups of different chain units or hydroxyl groups and water molecules, at the

expense of methoxy-methoxy interaction. The reduction of interfacial free energy by hydrogen bond has been reported for the bulk crystallized polyethylene oxide by *Booth, Bruce and Buggy* (27). σ_{ec} represents the sum of excess free energies for the sequence of less substituted units of a given MC chain which traversed the interfacial region. A high and negative value of σ_{ec} would have resulted if the interfacial region possessed a high negative enthalpy caused by the hydrogen bonding.

In conclusion, the inverted gelation of MC-water systems is also adequately predicted by the theory and the "cross linking loci" of MC gels consist of crystalline sequences of trimethyl glucose unit.

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Summary

The gel/sol transition temperatures (T_m^g) were measured by cooling of thermally reversible methyl cellulose (MC)-water gels using the ten MC samples. A linear relationship between $1/T_m^g$ and the logarithm of v_2x was found for each MC gel, where v_2 is the volume fraction of MC and x the degree of polymerization. The X-ray diffraction patterns of both MC films and gels revealed that the network junction points of the MC gels are crystalline and consist of trimethyl glucose units. The heat of fusion of trimethyl cellulose was estimated as 2.6×10^3 J/mol, and entropy of dilution parameter = -1.6 and $\Theta = 320$ K were also evaluated. Using these values, the gel/sol transition temperature was analysed according to our previous theory. It is concluded that the network junction points of MC gels are between 4 and 8 units long and also that the length is in good agreement with the sequence length estimated from the methoxy content of MC.

Zusammenfassung

Die Umwandlungstemperaturen (T_m^g) Gel/Sol von zehn Methylzelluloseproben (MC) wurden an dem Abkühlungsverhalten von reversiblen Methylzellulose-Wasser-Gelen untersucht. Ein linearer Zusammenhang zwischen $1/T_m^g$ und den logarithmischen v_2x -Werten wurde für jedes MC-Gel gefunden, worin v_2 die Volumenfraktion von MC und x den Polymerisationsgrad bedeuten. Die Röntgendiagramme von beiden, MC-Film und MC-Gel, weisen darauf hin, daß die Verzweigungspunkte vom MC-Gel Kristallite sind und diese aus Trimethylglucosegrundbausteinen aufgebaut werden. Die Schmelzwärme der Trimethylglucose

wurde zu 2.6×10^3 J/mol geschätzt, und der Wechselwirkungsparameter χ sowie die Theta-Temperatur wurden als $\chi = -1.6$ und $\Theta = 320$ K berechnet. Nimmt man diese Werte an, so kann man die Gel/Sol-Übergangstemperaturen nach unserer früheren Theorie bestimmen. Daraus läßt sich folgern, daß die Verzweigungspunkte von MC-Gel zwischen 4 und 8 Bausteinen lang sind und daß dies auch mit der bezüglichen Sequenzlänge, die aus dem Methoxygehalt abgeschätzt werden kann, übereinstimmt.

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