Melting Temperature of Thermally Reversible Gel. V. Heat of Fusion of Cellulose Triacetate and the Melting of Cellulose Diacetate–Benzyl Alcohol Gel

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ABSTRACT: The heat of fusion of cellulose triacetate was determined from the melting point depression to be $2360 \text{ cal mol}^{-1}$ (9.87 kJ mol^{-1}). The melting temperatures of thermally reversible gels of cellulose acetate in benzyl alcohol were measured over a range of polymer concentrations. The reciprocal of the gel melting temperature vs. $\ln v_2 x_w$ plot is linear, where v_2 is the polymer volume fraction in the gel and x_w is the weight-average degree of polymerization. The plot was analysed according to the thermodynamic theory of the melting of a gel and the crosslinking loci in the gel were inferred to be crystallites consist of triacetyl glucose units.

KEY WORDS Cellulose Triacetate / Cellulose Diacetate / Acetyl Cellulose /
Heat of Fusion / Gel / Sol–Gel Transition /

The sol–gel transition of secondary cellulose acetate has been receiving attention. The supramolecular structure of cellulose acetate gel is important for understanding the properties of cellulose acetate films prepared by the solvent cast and evaporation method, since the films are technically important for reverse osmosis. The thermally reversible gel formation of cellulose acetate in benzyl alcohol has been studied by several authors.^{1,2} Recently, Goebel and Berry³ investigated the supramolecular structure of the gel by light scattering and elasticity measurements. They concluded that the nonrandom character of the cross linking loci in the gel causes the small-angle light scattering. Furthermore, they estimated that the equivalent diameter D of the cross linking loci was $147 \text{ \AA}$ from low-angle X-ray scattering and the formation of the cross linking loci was attributed to the three dimensional nucleation process. However, the length of the crystallite could not be estimated.

In preceding papers of this series, one (AT) of the authors developed a thermodynamic theory for the melting of thermally reversible gels, assuming that cross linking locus is the crystallite of length ζ units.⁴ Despite that the melting point of gel is not the thermodynamic singularity,⁴ according to this

theory, the melting temperature of the gel (T_m^g) is given by

$$\frac{1}{T_m^g} = \frac{\zeta}{(\zeta \Delta h_u + \zeta B' V_A - 2\sigma_{ec})} \left(\frac{\Delta h_u}{T_m^0} + \frac{R V_A}{V_1} - R \ln X_A \right) - \frac{R}{(\zeta \Delta h_u + \zeta B' V_A - 2\sigma_{ec})} \ln v_2 x_w \quad (1)$$

In this equation, Δh_u is the heat of fusion per crystalline monomer unit, T_m^0 is the melting temperature of pure polymer, σ_{ec} is the end interfacial free energy of the crystallite, B' is the cohesive energy density of interaction between the crystalline unit A and the solvent medium which consists of a diluent and noncrystalline units, V_A , V_1 are the molar volumes of the crystalline unit and the solvent, respectively, v_2 is the volume fraction of the polymer in the gel, X_A is the mole fraction of crystalline unit and x_w is the weight-average degree of polymerization. Equation 1 has been applied to evaluate the crystalline length ζ and interfacial free energy σ_{ec} for many thermally reversible gels and ζ thus evaluated compared favorably with ζ values estimated by other methods such as spectroscopy, elasticity and swelling of gels.^{5,6,7}

The purpose of the present article is to evaluate ζ of the crystalline cross links in the cellulose acetate-benzyl alcohol gel and compare these values with the X-ray diffraction of gels. Not only through the study of melting of the gels, the Δh_u is also evaluated from the melting point depression of a cellulose triacetate-diluent system, since the Δh_u of cellulose triacetate has not yet been reported as far as we know.

EXPERIMENTAL

Materials

Daicel Cellulose Triacetate (hereafter abbreviated as CTA) was used. The degree of substitution was found to be 2.90. Daicel cellulose diacetate (hereafter abbreviated as CDA) was found to have a degree of substitution 2.55. The CDA was dissolved in acetone, fractionated at 296 K by adding ethanol as precipitant and ten fractions were obtained. Their intrinsic viscosities were determined in tetrahydrofuran and the molecular weight was determined by the viscosity equation

$$[\eta] = 7.46 \times 10^{-4} M_w^{0.672} \quad (2)$$

which was calculated by using Tanner and Berry's data.⁸ The acetyl content of each fraction was determined by the alkaline hydrolysis method. The characteristics of the samples used in this study are summarized in Table I.

Thermodynamic Property

The heat of fusion of CTA was estimated from the melting point depression of the CTA-diluent system. Dibutyl phthalate was selected as a diluent and the

melting points of the CTA-diluent mixtures were determined using a Perkin-Elmer differential scanning calorimeter Model IB. The weighted amount of CTA samples and the diluent were mixed by stirring in test tubes at 573 K, then slowly cooled to 293 K, and kept at this temperature for 24 h to crystallize the mixtures.

Melting Temperature and X-ray Diffraction of Gels

Gels of CDA-benzyl alcohol systems were prepared at 277 K for 43 hours in U-shaped tubes as described previously.⁴

The U-tubes were then heated at the rate 273.5 K min^{-1} and the temperature at which a pressure head caused flow through a fine capillary was employed as the melting temperature of the gels (T_m^g).

The X-ray diffraction patterns of CTA film cast from a methylene chloride-ethanol mixture (9:1), a CDA film cast from acetone and CDA gels (10 wt%) were obtained by a Rigaku Geigerflex SG-7.

RESULTS

X-ray Diffraction of CDA-Benzyl Alcohol Gel

The X-ray diffraction patterns of CTA, CDA and CDA-benzyl alcohol gel are compared in Figure 1 and the d -spacings are summarized in Table II. We

Figure 1. X-ray diffraction patterns of (A) a cellulose triacetate film, (B) a cellulose diacetate film, and (C) a film of cellulose diacetate-benzyl alcohol gel.

Table I. Characteristics of cellulose diacetate fractions

Sample No.	$[\eta]$ 100 ml g ⁻¹	M_w $\times 10^{-5}$	DP ^a	DS ^b
1	4.04	3.59	1391	2.29
2	3.59	3.01 ₅	1165	2.29 ₈
3	2.94	2.24	865	2.30 ₃
4	2.20	1.45 ₅	559	2.33 ₅
5	1.80	1.07 ₉	416	2.31
6	1.04	0.47 ₇	184	2.30

^a Degree of polymerization.

^b Degree of substitution.

Table II. Comparison of observed and calculated d spacings of CTA, CDA, and the CDA gel

	$2\theta/\text{deg}$	CTA FORM I		
		$d_{\text{obs}}/\text{\AA}$	$d/\text{\AA}$	(hkl)
CDA	9.2 (s)	9.60	9.56	$\bar{1}01$
	12.6 (m)	7.02	7.07	$\bar{1}11$
	17.7 (s)	5.01	5.07	012
CTA	9.9 (s)	8.93	8.89	201
	12.9 (m)	6.86	6.84	301
	17.6 (m)	5.03	5.07	012
	21.6 (m)	4.11	4.17	321
Gel	18.3 (s)	4.84	4.78	202

did not attempt to promote the crystallization of CTA and CDA films by stretching or rolling, since our purpose was only to compare the X-ray diffraction pattern of the gel with that of CTA and CDA films. Although the X-ray diffraction patterns of CTA and CDA films did not show high crystallinity, the patterns nevertheless indicate that the cellulose triacetate form I crystallites⁹ exist in the films. The X-ray pattern of the gel also exhibited very low crystallinity, corresponding to the CTA-I form. Therefore, the existence of small crystallites which perform the role of crosslinking loci clearly shown.

Figure 2. The DSC thermograms of cellulose triacetate-dibutyl phthalate systems. The v_2 indicates the volume fraction of the CTA in the mixtures.

Thermodynamic Properties

Since the presence of the crystalline crosslinks of cellulose triacetate form I was established, we needed to measure the heat of fusion of CTA, since this has not been reported. The melting temperature of CTA was reported as $T_m^0 = 579 \text{ K}$.¹⁰ The CTA sample was mixed with dibutyl phthalate and the melting point depression of the CTA was measured. The DSC thermograms shown in Figure 2 definitely show that the melting point depression increases with an increasing volume fraction of the diluent.

It is also noticed that the area under each DSC peak becomes smaller and smaller with increasing of the volume fraction of diluent. According to Flory,¹¹ the melting point depression of a polymer-diluent system is given by

$$\frac{1/T_m - 1/T_m^0}{v_1} = \frac{R}{\Delta h_u} \frac{V_u}{V_1} \left(1 - \frac{BV_1}{R} \frac{v_1}{T_m} \right) \quad (3)$$

where T_m^0 is the melting temperature of the pure polymer, Δh_u is the heat of fusion per monomer unit, v_1 is the volume fraction of diluent, V_u and V_1 are the molar volumes of a monomer unit and diluent, respectively, and B is the cohesive energy density. In Figure 3, $(1/T_m - 1/T_m^0)/v_1$ is plotted against v_1/T_m and a straight line is obtained. From the plot, we obtain $\Delta h_u = 2360 \text{ cal mol}^{-1}$ (9.87 kJ mol^{-1}) and $B = 5.4 \text{ cal ml}^{-1}$ (22.59 J cm^{-3}). Since the observed melting temperature of cellulose triacetate was 576 K which is almost identical with the literature value (579 K), the entropy of the fusion per monomer unit, ΔS_u , is equal to $4.09 \text{ cal mol}^{-1} \text{ deg}^{-1}$ ($17.11 \text{ J mol}^{-1} \text{ deg}^{-1}$). This value is about two thirds of the ΔS_u of cellulose tributyrate.¹²

Figure 3. The $(1/T_m - 1/T_m^0)/v_1$ vs. v_1/T_m plot.

Figure 4. The reciprocals of the gel melting temperature vs. $\ln v_2 x_w$ plots. Degrees of polymerization x_w : $\bigcirc$, 1391; $\square$, 1165; $\triangle$, 865; $\square$, 559; $\triangle$, 416; $\bigcirc$, 184.

Melting Temperature of Cellulose Acetate Gel

In Figure 4, the reciprocals of the gel melting temperature of CDA-benzyl alcohol gels are plotted against $\ln v_2 x_w$. The plot is linear and moreover almost independent of the molecular weight of CDA indicating that the Eldridge-Ferry like plot is applicable. This is understandable since the degree of substitution of the samples is almost the same in each case. The intercept of the plot is $3.08 \times 10^{-3} \text{ K}^{-1}$ and the slope is $3.38 \times 10^{-5} \text{ K}^{-1}$.

The interaction term B' was estimated by the relationship

$$A_2 = \frac{\bar{v}^2}{V_1} \left(\frac{1}{2} - \frac{B'V_1}{RT} \right) \quad (4)$$

where A_2 is the second virial coefficient, and $\bar{v}$ is the specific volume of CDA in solvent. Tanner and Berry⁸ reported that the value of A_2 of CDA is equal to $-2.013 \times 10^{-5} \text{ mol ml}^{-1} \text{ g}^{-2}$ in benzyl alcohol. Using eq 4, we obtain $B' = 3.167 \text{ cal ml}^{-1}$ (13.25 J cm^{-3}). Making use of $\Delta h_u = 2360 \text{ cal mol}^{-1}$ (9.87 kJ mol^{-1}); $T_m^0 = 579 \text{ K}$; $V_1 = 103.5 \text{ ml mol}^{-1}$ and $V_A = 182.0 \text{ ml mol}^{-1}$, and putting $X_A = \text{DS}/3$, the crystalline sequence length ζ of triacetyl glucose units and the interfacial free energy σ_{ec} are estimated from the above values of the intercept and the slope

by the procedure proposed previously.⁴ The results are shown in Table III and the length of the crystalline ζ is about 19 units and the interfacial free energy per crystalline sequence σ_{ec} is $2990 \text{ cal mol}^{-1}$ ($12.51 \text{ kJ mol}^{-1}$) of sequence.

DISCUSSION

The X-ray diffraction pattern of the CDA gel showed the presence of the crystalline order of the cellulose triacetate form I in the gel. The value of ζ indicates that small runs of triacetylglucose unit in CDA chains are responsible for this order. The occurrence of these triacetylglucose units is in consequence of the heterogeneous hydrolysis reaction of the CTA. Since the ζ is 19, the length of crystallite will then be $100 \text{ \AA}$, since the crystallite is the cellulose triacetate form I. Although our theory could not give the number of crystalline sequences in a crystallite, judging from the X-ray diffraction peak, there may be several such sequences.

From the X-ray small angle scattering of the cellulose diacetate-benzyl alcohol gel, Goeble and Berry³ estimated that the radius of gyration $\langle S^2 \rangle^{1/2}$ of the cross linking loci is $57 \text{ \AA}$ and that the effective diameter $D = 2 \cdot (5\langle S^2 \rangle/3)^{1/2}$ is $147 \text{ \AA}$. Although our estimation of the crystallite length is thermodynamic, the length of the crystallite $100 \text{ \AA}$ compared favorably with the estimated sizes of the cross linking loci. The effective diameter is about 1.5 times larger than our estimation. However, the size of the cross linking loci estimated by X-ray small angle scattering is considered to include not only the crystallite but also the amorphous chain sequences which emerge from the ends of the crystallite. Thus, the loci are the fringed micelle, making possible a large effective diameter. Consequently, we may say that both estimations, the X-ray small angle scattering method and the thermodynamic approach, are in reasonable agreement.

In conclusion, the gel melting temperature of the cellulose diacetate-benzyl alcohol gel can be predicted by the theory and the length of the "cross linking loci" of the gel is about $100 \text{ \AA}$.

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Table III. Experimental results and the estimation of ζ and σ_{ec}

Intercept $\times 10^3 \text{ K}^{-1}$	Slope $\times 10^5 \text{ K}^{-1}$	ζ	$\sigma_{ec} \times 10^{-3}$
			$\text{cal mol}^{-1}(\text{of sequence})^a$
3.08	3.38	18.5	2.9 ₉

^a $1 \text{ cal mol}^{-1} = 4.184 \text{ J mol}^{-1}$.

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