Thermal *cis–trans* Isomerization of Azo Dye Chrysophenine in Cellulose Matrices: Effect of Morphology

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SYNOPSIS

Films obtained from native cellulose synthesized by *Acetobacter xylinum* and from cellulose obtained from cuproammoniacal solutions (cellulose II) were morphologically characterized by studying the *cis-trans* isomerization of azo dye Chrysophenine dispersed in their amorphous region. The kinetic measurements of the reaction showed that both films behave as glassy polymers in the temperature range explored (36–66°C). In going from native cellulose to cuproammoniacal cellulose, an increase of the isomerization rate was observed, revealing a more homogeneous distribution and likely larger extent of free volume in the amorphous phase of cellulose II.

INTRODUCTION

In previous works[1–6] we studied the kinetics of thermal *cis–trans* isomerization of some azo dyes in order to characterize the supermolecular structure of the polymers in which they were dispersed.

The different kinetic behaviors observed for the various dyes investigated were correlated to the different microenvironments of the dyes in the amorphous regions of the polymer matrix.

Solid dyed films of semicrystalline rubber and glass polymers were investigated below and above the glass transition temperature (T_g).

The studies were carried out using 4-diethylaminoazobenzene derivates, and the effect of polarity, viscosity, and other rheological properties of liquid polymers on the thermal *cis–trans* isomerization of the azo group were also investigated.[3,4]

The aim of this work is to characterize morphologically cellulose, a polymer with a well-known molecular structure but not fully defined as regards the behavior of its amorphous phase. In fact, cellulose can be considered a highly crystalline hydroplastic polymer in which internal water acts as a plasticizer thus determining the glass transition temperature.[7]

In order to perform this study, light transparent cellulose samples for visible absorbance measurements and azo dyes with measurable isomerization kinetics in the cellulose hydrophilic medium had to be used.

Films obtained either from cellulose synthesized by *Acetobacter xylinum* or from cellulose obtained from cuproammoniacal solutions are transparent, unlike vegetal native cellulose films (that lack this characteristic).

As far as dyes are concerned, C. I. Direct Yellow 12 (Chrysophenine) was used for its characteristic to isomerize in a water medium with measurable reaction rate.

EXPERIMENTAL

Materials

Native Cellulose by Acetobacter xylinum

Acetobacter xylinum ATCC 10821, a rod-shaped gram-negative bacterium, was grown at 28°C without shaking on a culture medium (YEFD) containing 2% bactopeptone (DIFCO No. 0118-01-8), 1% yeast extract (DIFCO No. 0127-01), 2% anhydrous glucose (Carlo Erba FU), 2% bactoagar (DIFCO No. 0140-01) when needed, and a pH of 5.5. Transfers were made every 30 days.

The cellulose material synthesized, obtained after at least 8 days of growth, was separated from the culture medium and the bacteria by washing with a solution of 2% sodium hydroxide at 70°C, until the turbidity, caused by the bacteria, disappeared.

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The pH was adjusted to 7.0 with deionized water and 0.5% acetic acid.[9]

The extended polyglucosan chains of never-dryed cellulose are surrounded by layers of water molecules. The cellulose gel was dehydrated by evaporation to obtain the change from gel to film by irreversible formation of hydrogen bonds between hydroxyl groups.[10]

Using a scanning electron microscope operating at 5–20 Kv, the surface of native dried cellulose shadowed with gold and cellulose gel samples prepared by critical point drying method were examined. In both these materials the macrofibrils are randomly dispersed and therefore they look to be "as isotropic" materials made up of anisotropic elements (microfibrils).

Wide angle X-ray diffraction measurements showed the typical diffraction profile of native cellulose.

Infrared (IR) characterization of the cellulose films was performed on a Perkin-Elmer Model 983 IR spectrophotometer. Infrared spectrophotometry of native cellulose showed no dichroism in an unstretched condition, but stretched material had an appreciable dichroic index. This investigation was done with peaks at 1336 and 1428 nm, the first for the perpendicular dichroism of the OH group and the second for the parallel dichroism of the CH_2 group.

Cellulose material obtained by the cuproammoniacal method[11] was used to prepare films of cellulose II that are light transparent.

Film dyeing was carried out with 1% of dyestuff, calculated on the volume of the tinctorial bath. The process was started at 30°C, raising the temperature to 80°C in 30 min and keeping this temperature for 30 min. Film dye concentration was chosen to obtain an absorbance near 0.5 for isomerization measurements.

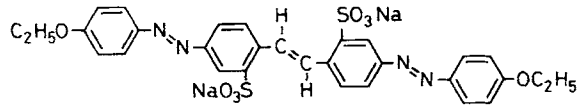
To dye the cellulose film we used Chrysophenine (C. I. 24895, Direct Yellow 12) purchased from Aldrich Chemical Company Inc. (Milwaukee, WI).

Measurements

The polymer films dyed as described were sandwiched between two quartz plates and exposed for 15 min in a thermostated compartment to the light of a 200-W tungsten lamp, a long enough time to reach a photostationary state. After irradiation the film was quickly introduced in the cell compartment of a Jasco Uvidec 320 spectrophotometer thermostated at the same temperature of the irradiation (in the range of 36–66°C). The thermal return was monitored as the change in absorbance at the wavelength corresponding to the absorption maximum of the *trans* isomer (422 nm).

RESULTS

The dye used is Chrysophenine:



It presents a suitable spectroscopic behavior during the isomerization reaction in water[8] unlike other direct acid and reactive dyes and a sufficient tinctorial capacity on *Acetobacter xylinum* cellulose not obtainable using monoazo disperse dyes.

Chrysophenine was dispersed in cellulose film characterized by a degree of polymerization DP = 1600 (native cellulose) and DP = 600 (cellulose II).

The kinetics of the thermal *cis–trans* isomerization of cellulose films could be resolved as the sum of two or three simultaneous first-order processes, according to a procedure previously described,[1,2] namely by extrapolating the linear portion of the curve of $(A_\infty - A_t)$ versus time t (where A_∞ and A_t are the absorbance at infinite time and at time t, respectively) to zero time, by a least-squares fit with a correlation $r > 0.99$. In this way the rate constant of a first-order reaction is obtained. From the difference between experimental curve and the extrapolated line, the linear time dependence of another first-order reaction was obtained.[12] This procedure may be extended to a third reaction. An example of this treatment of experimental data is reported in Figure 1.

The isomerization was studied in the temperature range of 36–66°C. The value of E_{max} (π, π^*) for the visible absorption band of Chrysophenine in both cellulosic films was 67.5 kcal/mol.

The activation parameters of the single processes are reported in Table I. The average fractions of dye that isomerize according to the simultaneous first-order reactions 1, 2, and 3 (r_1, r_2, and r_3) are collected in Table II.

In the same table the range values of the term $\Delta A/A_\infty$ that measures the absorbance amplitude covered during kinetic measurements relative to the absorbance at infinity are reported in order to take into account the different concentration of the dye. These values are related to the temperature range ΔT examined.

The values of the mean relaxation time, τ, at 36°C of the *cis–trans* isomerization of Chrysophenine in both cellulose films are as follows:

Table I Rate Constants at 36°C and Activation Parameters for the Thermal *cis–trans* Isomerization of Chrysophenine in Films of Native Cellulose from *Acetobacter xylinum* and Cellulose II Films

	Reaction 1	Reaction 2	Reaction 3
Film XNC[a]			
10^5 k/s^{-1}	3.64	66.0	480
ΔH^*/kcal mol^{-1}	18.3 ± 3.8	17.8 ± 3.5	18.9 ± 2.5
ΔS^*/e.u.	−19.9 ± 11.6	−15.5 ± 10.8	−8.2 ± 7.7
Film C.II[b]			
10^5 k/s^{-1}	10.4	73.6	
ΔH^*/kcal mol^{-1}	14.0 ± 1.8	17.2 ± 1.3	
ΔS^*/e.u.	−31.4 ± 5.5	−17.3 ± 3.9	

[a] Native cellulose by *Acetobacter xylinum*.
[b] Cuproammoniacal cellulose (cellulose II).

Film	$10^{-4}\ \tau/s$
Native cellulose by *Acetobacter xylinum*	1.28
Cellulose II	0.36

In order to verify the influence of acidity of medium on the *cis–trans* isomerization of Chrysophenine, some kinetic measurements were carried out in water solutions at different pH values. The corresponding kinetic constants and the activation parameters are reported in Table III.

DISCUSSION

The scanning electron microscope analysis carried out on native cellulose synthesized by *Acetobacter xylinum* shows that the film may be considered as an isotropic material because the macrofibrils, even if made up of anisotropic microfibrils, are randomly arranged. This kind of structure was confirmed by X-ray diffraction and IR analysis as described under Materials.

The native cellulose film has a complex structure characterized by regions with different lateral order in which the cellulosic macromolecules are partially oriented in the direction of growth axis.

The cuproammoniacal cellulose films (cellulose II), as well as all regenerated cellulose films, have a different supermolecular structure compared to the native cellulose. As it is known, cellulose II has a different crystalline lattice and a lower polymerization degree. Moreover, during the dissolution, the macromolecules may move freely inside the solvent so that they lose, at least partly, their linear configuration, and afterward they regenerated in an entangled structure in the amorphous region that results isotropic in the absence of stretching conditions.

Indeed, in the cellulose gel obtained from *Acetobacter xylinum*, the microfibrils, owing to the high number of hydrogen bonds, present a very stable entropic situation (even though lower than in cellulose II) so that the supermolecular order cannot be destroyed mechanically, and it is not possible to convert native cellulose into cellulose II. This trans-

Table II Average Weights of the Thermal Relaxation Processes of Chrysophenine in Cellulose Films, Observed in the Temperature Range ΔT and Extents of the Absorbance Amplitudes Covered During the Overall Reaction

Film	r_1	r_2	r_3	ΔT (°C)	$\Delta A/A_\infty$
XNC[a]	0.424	0.414	0.162	36–66	0.97
C.II[b]	0.276	0.724		36–66	0.94

[a] Native cellulose by *Acetobacter xylinum*.
[b] Cuproammoniacal cellulose (cellulose II).

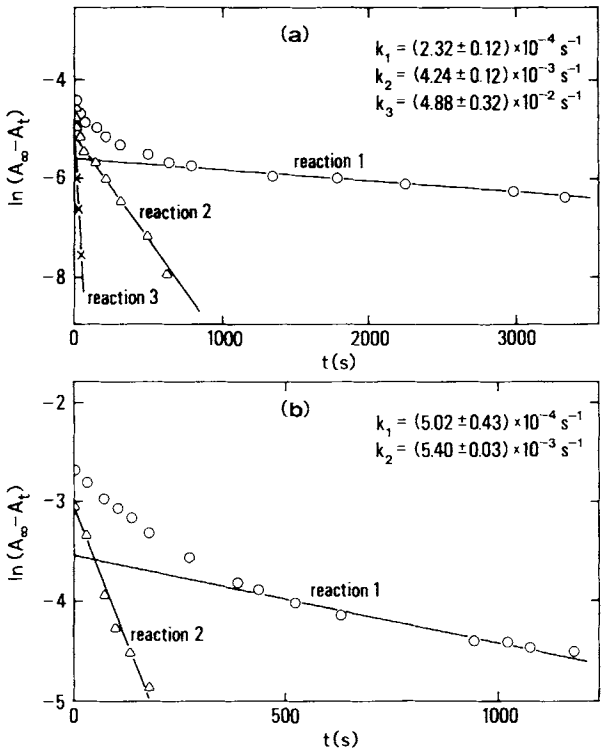


Figure 1 Resolution of the thermal *cis–trans* isomerization of Chrysophenine in (a) native cellulose and (b) cellulose II at 60°C using first-order reactions; A_∞, A_t, absorbance at 422 nm at infinity time and at time t, respectively. (○), experimental values; (△) and (×), values obtained according to the procedure described in previous works.[1,2]

formation needs, as it is known, a chemical action of dissolution.

In line with the findings of our previous works,[1,2,5,6] also in cellulose films the hypothesis has been verified that the *cis–trans* isomerization kinetics of a dye depends on the microstructure of the amorphous region of the polymer (Tables I and II). In fact, it was found a significant change of such kinetics, reasonably due to a free-volume modification in going from native cellulose to cellulose II.

The occurrence of two or three simultaneous first-order reactions shows that in the working conditions in the temperature range 36–66°C and in the relative humidity range 8.0–8.2%, the cellulose behaves as a glassy polymer.

The occurrence of three first-order reactions for the dye dispersed in the amorphous region of native cellulose and of only two for the same dye in cellulose II, could be explained by considering that the relative order of the native cellulose microfibrils, producing a greater packing in the amorphous structure, gives rise to a multiplicity of very distinct states, higher than those of cellulose II.

In fact, in the case of cellulose II the dissolution process, causing a higher isotropy of the amorphous region, levels the degree of free-volume distribution in the different states.

In contrast with the dyes studied in previous work, Chrysophenine may isomerize at three different positions, namely the two azo linkages and the carbon–carbon double bond. In principle this could give rise to the observed relaxation spectrum. However, as far as the azo group is concerned, the symmetry of the molecule is likely to prevent any relaxation multiplicity, while comparison with stilbenes shows that isomerization of the carbon–carbon double bond is generally more difficult than azo nitrogen inversion.[13,14] This is also confirmed by the behavior of Chrysophenine in water solution where a single first-order process is always observed.

Finally, it is well known that *cis–trans* isomerization of azo compounds is strongly affected by acid catalysis;[15,16] therefore, in order to rule out influences of local acidity changes in the membrane, experiments were also performed in water solution at various pH in the range 4–9, and no substantial variations were found (Table III). Lower pH were not used in order to avoid the presence of protonated species.[17]

CONCLUSION

The kinetic measurements of the *cis–trans* isomerization of Chrysophenine in the samples under in-

Table III Rate Constants at 36°C and Activation Parameters for the Thermal *cis–trans* Isomerization of Chrysophenine in Water at Different pH Values

pH	E_{max} (π, π^*), kcal/mol	10^5 k(s^{-1})	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ e.u.
4	71.8	27.3	17.7 ± 0.8	17.7 ± 2.5
7	71.4	27.7	18.9 ± 1.7	13.9 ± 5.1
9	71.1	22.8	18.8 ± 0.5	14.3 ± 1.0

vestigation show that the cellulose synthesized by *Acetobacter xylinum* and cellulose II behave as a glassy polymer in the temperature range explored ($> 36°C$) provided that the equilibrium relative humidity is maintained.

In going from native cellulose to cellulose II a significant increase of the *cis–trans* isomerization rate is observed in correspondence with a more homogeneous distribution and likely larger extent of free volume in amorphous phase of cuproammoniacal cellulose.

The less leveled free-volume distribution in the case of native cellulose is confirmed by the higher reaction multiplicity inside this matrix.

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