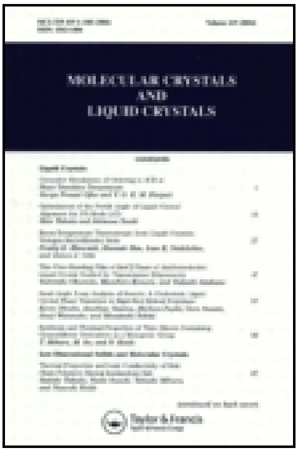

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Amorphous-Crystal Transition of Organic Dye Assemblies 2: Thermal Properties of Steroids Used in Rewritable Color Recording Media

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AMORPHOUS–CRYSTAL TRANSITION OF ORGANIC DYE ASSEMBLIES 2: THERMAL PROPERTIES OF STEROIDS USED IN REWRITABLE COLOR RECORDING MEDIA

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Abstract The relationship between molecular structures and amorphous thermal properties of some steroids were investigated in the design of rewritable color recording media. Amorphous states with a high glass transition temperature (T_g) were produced from steroids with plural hydrogen–bonding sites separated. Rapid crystallization was observed for steroids with a hydrogen–bonding site or without a flexible alkyl chain. Polymorphism of crystals is also discussed.

INTRODUCTION

Nonpolymeric amorphous dyes have attracted much attention because of their potential applications,for examples, as electroluminescent devices.[1] For these applications, heat resistivity is required. In previous papers,[2,3] we established the theoretical relationship between the thermodynamic parameters of phase transitions and amorphous thermal properties such as glass transition temperature (T_g), maximum crystallization velocity (*MCV*) and crystallization temperature (T_c). Furthermore, we developed a molecular design rule to control these amorphous properties.

As one of the applications, we have reported on a new rewritable color recording media using an amorphous–crystal transition.[4] Rewritable color media are expected to be environmentally beneficial because they would save on cards, office paper and OHP sheets, and by offering superior functionality, they would give rise to a new market. One of our media consisted of a color former (leuco dye), a developer (phenol compound) and reversible matrix (steroid). The amorphous state of the media was colorless and the crystalline state was colored. Another type of media was composed of a color former and a developer serving for a reversible matrix (steroid with a phenol group).

The present paper describes the relationship between the molecular structures of the steroids and their amorphous thermal properties according to the molecular design rule.[2,3]

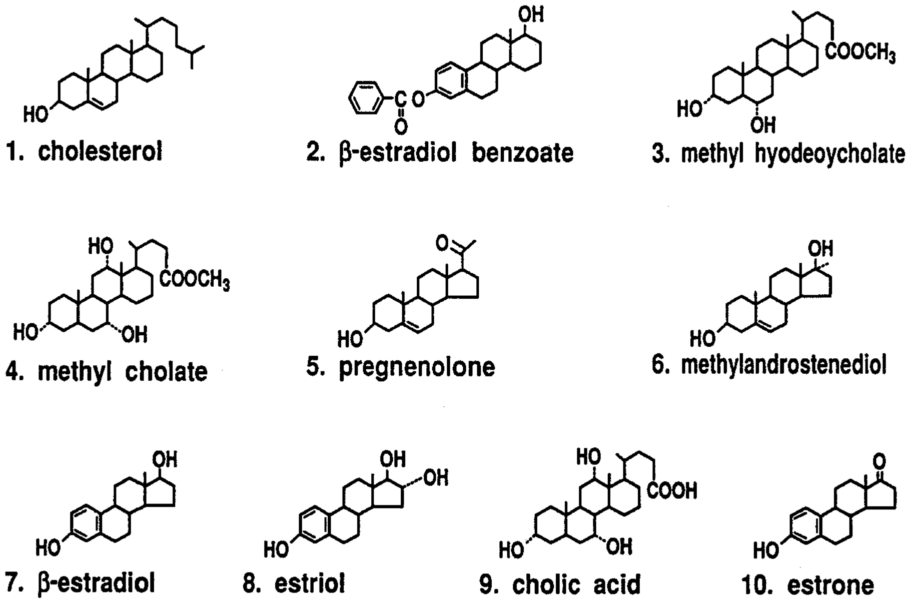
EXPERIMENTAL SECTION

Materials

Figure 1 shows the molecular structures of the steroids used in this study. They were purchased from Tokyo Kasei (Japan) and used without further purification.

Thermal Analysis

Thermal properties were determined by differential scanning calorimetry (DSC) using a Du Pont 990 thermal analyzer. Samples of 5–20 mg in polycrystalline form were put in aluminum pans and heated at a scan rate of 5 deg/min under a nitrogen flow.



1. cholesterol 2. β-estradiol benzoate 3. methyl hyodeoycholate
4. methyl cholate 5. pregnenolone 6. methylandrostenediol
7. β-estradiol 8. estriol 9. cholic acid 10. estrone

FIGURE 1. The molecular structures of the steroids used in this study.

RESULTS AND DISCUSSION

Glass Transition Temperature (T_g)

Table I indicates the thermal data for the amorphous states of the steroids. Figure 2 shows the relationship between T_g and transition–fusion entropies. T_g can be described by the following theoretical equation:[3] $T_g = h_g/(\Sigma\Delta S_{tr,m}/N)$, where h_g is a material family constant, $\Sigma\Delta S_{tr,m}$ is the sum of the entropies of fusion and of phase transitions between (T_g/K) and the melting point (T_m/K), and N is the number of heavy atoms per molecule, except hydrogen atoms. h_g values are large for high network–forming materials. Steroids with a hydrogen–bonding site (cholesterol, β–estradiol benzoate) and steroids with plural hydrogen–bonding sites located nearby (methyl hyodeoxycholate, methyl cholate) gave the plots (closed circles) on the theoretical curve (h_g = 0.8 kJ/mol) for aromatic compounds without a hydrogen-bonding site (open circles). The plots (closed diamonds) for the other steroids with plural hydrogen-bonding sites separated are located in a higher T_g region because of higher h_g values. Intermolecular networks are formed in the latter steroids. Steroids with a high T_g produced a rewritable recording media with a high T_g. Records remained stable for a long time below T_g.

TABLE I Thermal data for some steroids

No.	Compound	T_m(K)	T_g(K)	N	$\Delta S_m/N$ (J/K mol)	$\Sigma\Delta S_{tr}/N$ (J/K mol)	T_{c1}(K)	$N/(T_m\Sigma\Delta H_{tr,m})$ (mol/K kJ)
1	cholesterol	418	301	28	2.51	0.36[a]	306	0.0021
2	β-estradiol benzoate	463	325	28	2.43	0	359	0.0019
3	methyl hyodeoxycholate	400	327	29	0.89	1.20[b]	n.o.[c]	0.0030
4	methyl cholate	470	388	29	3.01	0	n.o.	0.0024
5	pregnenolone	461	331	23	3.34	0.40[d]	343	0.0013
6	methylandrostenediol	476	343	22	3.69	0	362	0.0012
7	β-estradiol	447	349	20	2.74	0	398	0.0018
8	estriol	550	371	21	3.77	0	398	0.0009
9	cholic acid	470	388	29	3.01	0	n.o.	0.0015
10	estrone	525	n.a.[e]	20	2.67	0.29		0.0012

[a] T_{tr} = 307 K. [b] T_{tr} = 390 K. [c] not observed. [d] T_{tr} = 449 K. [e] Amorphous was not obtained.

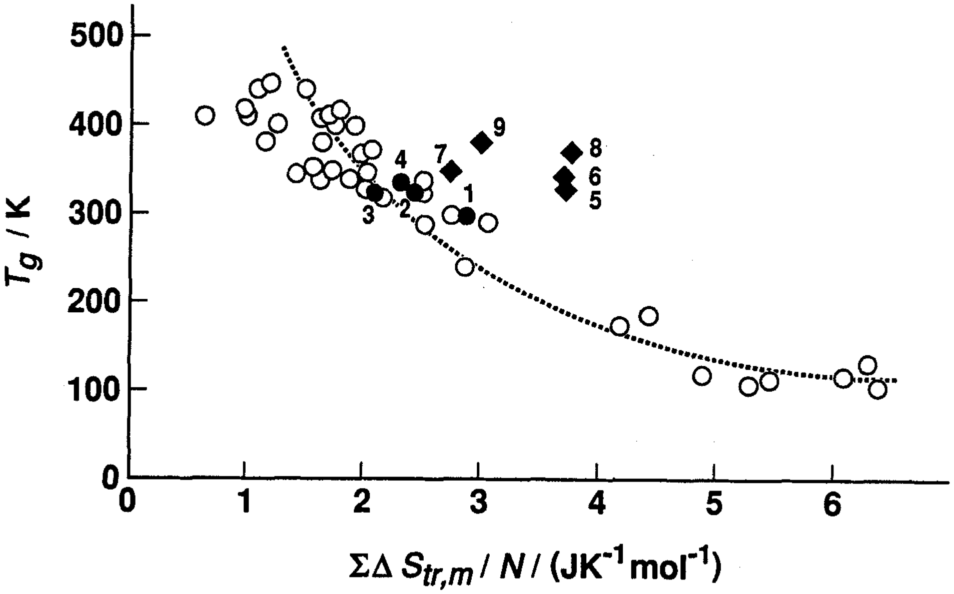


FIGURE 2. Relationship between glass transition temperature (T_g) and transition-fusion entropies ($\Sigma\Delta S_{tr,m}/N$) for steroids with a hydrogen-bonding site or with plural hydrogen-bonding sites located nearby (●), for steroids with plural hydrogen-bonding sites separated (◆), and for aromatic compounds without a hydrogen-bonding site (○). The dotted line indicates the theoretical curve: $T_g = h_g/(\Sigma\Delta S_{tr,m}/N)$, h_g = 0.8 kJ/mol.

Crystallization

A maximum crystal–growth velocity (*MCV*) is one of the most important parameters for amorphous formation and for crystallization. A low *MCV* value indicates an easy amorphous formation by cooling a fusion and indicates a slow crystallization. *MCV* can be described by the following theoretical equation:[3] $MCV = k_0\exp[h_{mc}N/(T_m\Sigma\Delta H_{tr,m})]$, where k_0 is a constant, h_{mc} is a material family constant, and $\Sigma\Delta H_{tr,m}$ is the sum of the enthalpies of fusion and of phase transitions between a maximum crystal–growth temperature ($T_{c,max}$) and T_m. The h_{mc} value increases as the network degree increases along with the h_g value. According to Table I and Fig.2, an *MCV* value can be considered to decrease in the following order because $N/(T_m\Sigma\Delta H_{tr,m})$ increases in the same order with a constant h_{mc} value: β–estradiol benzoate, cholesterol, methyl cholate and methyl hyodeoxycholate. The latter two steroids showed no crystallization in the DSC measurement. For the steroids with plural hydrogen–bonding sites separated, *MCV* can be roughly predicted to decrease in the following order: estriol, estrone, methylandrostenediol, pregnenolone, cholic acid and β–estradiol. The order was mostly consistent with the experimental results. Rapid crystallization required for the recording media has been obtained from the steroids with a hydrogen–bonding site or without a flexible alkyl chain.

Polymorphism of Crystal

High T_g and low T_m are required for the rewritable recording media from the viewpoint of thermal stability of a record and of energy saving. However, the following rule of thumb has been established: $T_g = 2/3\cdot T_m$. One of the solutions to the inconsistent requirement (high T_g, low T_m) is using the polymorphism of crystals, because T_m in the above equation corresponds to the highest melting point. Figure 3 shows the DSC charts of β–estradiol benzoate and of the rewritable medium consisted of crystal violet lactone, propyl gallate and β–estradiol benzoate (1:1:10 in weight–%). The amorphous state of β–estadiol benzoate showed T_g at 52°C, and crystallized at T_{c1}. The resulting crystal melted at T_{m1}, and immediately crystallized to produce another crystalline state, which melted at T_{m2}.

The amorphous state of the recording medium showed T_g at 52°C, and crystallized at T'_{c1} ($>T_{c1}$). The resulting crystal melted at T'_{m1}. The second crystallization and the second melting were scarcely observed, because the second crystallization rate was slow compared with the heating rate. At a slow heating rate, the second crystallization peak was observed. For the recording media, rapid heating by a thermal printer head or by a hot stamp is applied. Therefore, the apparently beneficial low melting temperature was obtained.

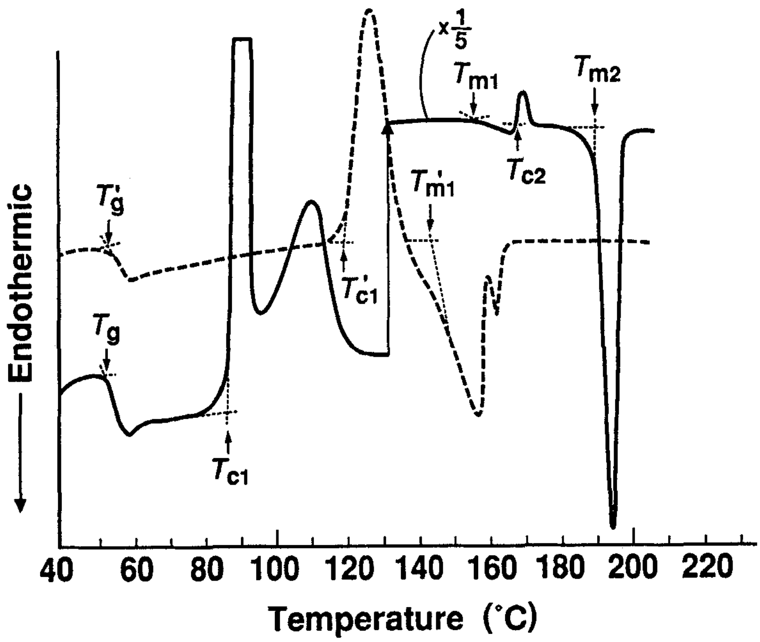


FIGURE 3. DSC charts for β-estradiol benzoate (——), and for a rewritable recoding medium consisting of crystal violet lactone, propyl gallate and estradiol benzoate (1:1:10 in weight-%) (- - - -).

CONCLUSION

The relationship between the molecular structures of the steroids and their amorphous thermal properties have been rationalized by using theoretical equations involving thermodynamic parameters. The polymorphism of crystals of β-estradiol benzoate is advantageous for reducing the apparent melting temperature.

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