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Glass-forming organic radical compounds with cholesterol and benzylideneamine cores

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Abstract—Several organic radical compounds based on TEMPO radical with cholesterol and benzylideneamine cores (3a-c) were prepared. The radical compounds were found to freeze into glassy state when cooled from their isotropic liquid state and characteristic heat-responsive magnetic properties were observed in the radicals due to the phase transitions. © 2005 Elsevier Ltd. All rights reserved.

To the development of novel organic spin systems with multi-property significant attention is paid in the field of materials chemistry and among them spin systems with photo-functionality have recently been explored in this respect rather extensively.¹ The preparation of organic spin system with liquid crystalline² and/or heat-responsive property is also attractive because of the possibility of the alternation of magnetic property through the phase transition and we hence, prepared so far several organic radical compounds like 1 or 2 and found significant changes of the magnetic properties in a couple of compounds (1: $R = CH_3(CH_2)_6$ and **2b**) owing to their phase transitions.³ In this letter, we wish to report the preparation of glass-forming organic radical compounds based on TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) with cholesterol and benzylideneamine cores (3a-c) (Chart 1) and the changes of their intermolecular magnetic interactions through the thermal phase transitions. Since glassy materials offer some advantage in processing into films without grain boundaries as often observed in crystalline materials, they are thought to have potentials for advanced technology⁴ and, to our knowledge, no distinctly glass-forming organic radical has so far been reported.

The preparation of the radical compounds **3a–c** was carried out as shown in Scheme 1. Cholesteryl bromoalkanoates $(4a-c)^5$ prepared by treating commercial optically pure cholesterol with bromoalkanoyl chlorides were reacted with 4-hydroxybenzaldehyde under a mild basic reaction condition to give the corresponding benzaldehyde derivatives with a cholesterol unit (**5a–c**) in 71– 77% yield. After several unsuccessful trials, presumably because of the gel formation with the solvents used, the aldehydes could be converted to the corresponding Schiff bases **3a–c** by heating with 4-amino-TEMPO in benzene or toluene for prolonged time (2–4 days) with the yields (after recrystallization from appropriate solvents) shown in Scheme 1.⁶

The liquid crystal property of aldehyde derivatives 5a-c was evidenced with the help of optical polarizing microscopic and calorimetric studies. These compounds were found to exhibit smectic A (SmA) and/or chiral nematic (N*) phases.⁷ On the contrary, surprisingly, no mesomorphic behavior could be discerned for the radical compounds 3a-c. However, interestingly, these crystalline materials were found to form glassy films when cooled from their isotropic liquid state that was ascertained based on optical and calorimetric studies. Radical compounds 3a and 3b form the glassy films (vitrification) either by rapid (quenching at 5–10 °C) or by slow cooling at a rate of 2–10 °C/min, whereas for 3c vitrification was achieved only by rapid cooling from

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Chart 1.



Scheme 1. Reagents and conditions: (i) anhyd K₂CO₃, DMF, 85 °C, 16 h; (ii) 4-aminoTEMPO, benzene, or toluene, reflux, 2-4 days.

its isotropic liquid state, which otherwise reverts to crystalline state when cooled slowly. In other words, these compounds while cooling from their liquid state (melting point) fail to show the transition to crystal state, instead, they freeze into glassy state that is characterized by their superior optical quality (transparent) over a large domain with no grain boundary and therefore, in our opinion have potentials for advanced technology.⁴ This behavior is quite remarkable given the fact that these systems are low molar mass magnetically active compounds with glassy film forming capabilities, which otherwise is ubiquitous among polymeric systems. The lack of liquid crystalline nature in the radicals 3a-c may be attributed to the existence of bulky tetra-methyl groups around the spin center, being detrimental for the formation of ordered molecular aggregates. Since apparent phase transitions into the glassy states were observed in the radicals, the temperature dependence of their magnetic susceptibilities was measured from 2 to ca. 400 K (over their melting points) by using SQUID susceptometer. As a typical example, the $\chi T-T$ profile for **3b** is shown in Figure 1 and the data for heating/cooling processes of the radicals **3a-c** are summarized in Table 1.8 Thus, the γT values of the radical **3b** deviate gradually from Curie–Weiss law increasing over 350 K, which in turn decrease abruptly over the phase transition temperature at around 388 K (115 °C). Although the reason is not clear yet, antiferromagnetic interaction is apparently intensified in the glassy state of this radical during



Figure 1. $\chi T-T$ profile (heating/cooling) of the radical 3b between 2 and 400 K.

the cooling process. It is generally seen within the three radicals that the Curie constants as well as Weiss temperatures decrease in the cooling process after melting to the glassy state (Table 1).⁸ Among them, weak ferromagnetic interaction observed in the heating process of the compound **3a** was found to turn to antiferromagnetic nature is preserved on the whole for the other two radicals **3b,c** with the longer paraffinic central spacer in spite of the difference of their Curie constants and Weiss temperatures. Thus, characteristic heat-responsive mag-

Table 1. Magnetic data, phase transition temperatures (°C) and enthalpies (J/g) of 3a-c

Compds	Process	Magnetic interaction ^a	$C^{\rm b}$ /emu K mol ⁻¹	$\theta^{\rm c}/{\rm K}$	Phase transition ^d
3a	Heating	Ferro	0.29	0.09	Cr 100.5 (25.1) Iso
3a	Cooling	Antiferro	0.26	-0.27	Iso 56 ^e Tg ^f
3b	Heating	Antiferro	0.37	-0.90	Cr 115.5 (33.9) Iso
3b	Cooling	Antiferro	0.32	-0.37	Iso 82 ^e Tg ^f
3c	Heating	Antiferro	0.27	-0.86	Cr ^g 107.3 (28.6) Iso
3c	Cooling	Antiferro	0.25	-0.40	Iso 45.8 (0.5) Cr or Iso 5 Tg ^h

Cr = Crystal; Iso = isotropic phase; Tg = glassy state.

^a Fitted by using the Curie–Weiss law.

^bCurie constant.

^cWeiss temperature.

^d Peak temperatures in the DSC thermograms obtained during the first heating and cooling cycles at a rate of 5 °C/min.

^eObserved under microscope and too weak to get recognized in DSC.

 $^{\rm f} \, Exists$ till $-60 \ ^{\rm o} C$ in which the Iso state is freezed.

^g An additional Cr–Cr transition was observed at 91.5 °C (3.3 J/g).

^h Vitrification occurs upon rapid cooling.

netic properties were observed in the radical compounds due to the phase transitions.

We are currently making efforts to prepare related compounds, such as the ones with salicylideneamine⁹ instead of benzylideneamine or Cu(hfac)₂ complexes with two radical units¹⁰ and the details of the experimental results will be reported in future.

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- 6. The radical compounds **3a**-c were characterized by elemental analysis and spectroscopic data.
- 7. Details of the liquid crystalline properties of **5a-c** will be reported elsewhere.
- 8. Although we have no concrete evidence to explain the smaller values of the Curie constants of the radicals than the theoretical ones (0.375 emu K mol⁻¹, g = 2.0033), it might be due to a partial decomposition of the radicals during handlings and/or contamination of diamagnetic impurities.
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