Journal of Thermal Analysis and Calorimetry, Vol. 63 (2001) 663–669

PHASE DIAGRAMS OF PERHYDROTRIPHENYLENE AND AROMATIC COMPOUNDS
II. Terthiophene and related thiophene oligomers

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(Received October 19, 2000)

Abstract

Terthiophene included in a perhydrotriphenylene (*PHTP*) adduct exhibits an UV spectrum different from that observed in the bulk or in solution. The X-ray diffraction pattern also differs significantly from that of pure *PHTP*. The UV spectrum is interpreted as due to an isolated molecule in a vacuum-like space, in agreement with a model developed from X-ray diffraction data. Knowledge of the phase diagram was essential for an interpretation of the optical properties and of some kinetic aspects of the formation of the inclusion compound phase. In this work, the phase diagrams of terthiophene (*T3*) are presented, and DSC evidence of the inclusion of quater- (*T4*), penta- (*T5*) and α,ω-dihexylquaterthiophene (*DH4T*) is discussed.

Keywords: inclusion compounds, perhydrotriphenylene, phase diagrams, quater-, penta- and α,ω-dihexylquaterthiophene

Introduction

In previous works, we discussed the phase diagrams of perhydrotriphenylene (*PHTP*) with guest molecules of different sizes and polarities, such as *trans*-stilbene and 4H-cyclopenta(2,1-b:3,4-b')dithiophene [1]. The starting point of the present work was the study of the UV spectrum of terthiophene in solution, in the bulk and in the solid state, as included in its adduct with *PHTP* [2–7]. The idea was that, as observed in the inclusion polymerization of diene monomers, the guest can form a long series of molecules in the channel, each series being isolated from the others by the hydrocarbon channel walls [8]. In this way, the differences measured in the UV spectra are consistent with suppression of the strong interactions of π-systems of different guest molecules present in the bulk. Determination of the presence and purity of the adduct phase is possible only when the phase diagram of *PHTP*/guest mixtures is determined.

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1418–2874/2001/ $ 5.00
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Several such examples have been determined by our group [9]. Crystal structures of *PHTP* adducts of push-pull molecules have been reported by Hulliger *et al.* [10].

The present paper is mainly devoted to determination of the phase diagram of terthiophene/*PHTP* mixtures. DSC evidence of the presence of *PHTP* adducts is also presented for higher thiophene oligomers.

Materials and methods

PHTP (Fig. 1) was synthesized according to the literature [11]; the adduct with *n*-heptane was used for separation of the *anti-trans-anti-trans-anti-trans* isomer from other stereoisomers; thermal decomposition of the *PHTP*/*n*-heptane inclusion compound produces pure *PHTP*. The guests were Fluka products (used without further purification), or their synthesis was reported previously. DSC analyses were run on Mettler TA 3000 or DSC 820 instruments. The solidus temperature (T_S) was measured at the peak temperature of isothermal melting of the eutectic; the liquidus temperature of mixtures (T_L) was determined at 95% of the integral curve by using the liquid fraction routine.

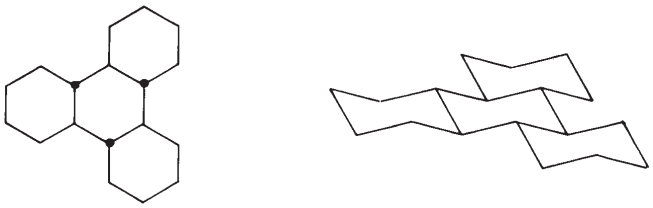

Fig. 1 Structure of *PHTP*

Results and discussion

Inclusion compounds are binary compounds that undergo congruent or incongruent melting and incongruent vaporization, as discussed by Roozeboom [12] and van der Waals [13]. The analysis of the phase diagrams is reported in the classical book by Ricci [14]. In the organic field, systematic studies relating to inclusion polymerization were reported by Farina's group for *PHTP* adducts relating to inclusion polymerization [15].

The phase diagram of mixtures of two molecules forming an inclusion compound can be derived by overlapping two different phase diagrams: the first is due to the guest (A) and to the adduct (C), and the second to C and the host molecule (B). The two diagrams overlap at the composition of the pure adduct (x_{OB}). The resulting diagram (Fig. 2) is described by van't Hoff and Prigogine [16] with the hypotheses of a) immiscibility in the solid phase, b) the adduct is not present in the liquid phase and c) ideality is observed in the liquid phase.

With these hypotheses, Farina and Di Silvestro developed equations (Eqs (1–3)) for *PHTP* inclusion compounds [17].

$$\ln(1-x)+n\ln x=$$
$$-\frac{\Delta H_c}{RT}+\frac{\Delta H_c}{RT_c}+n\ln n-(n+1)\ln(n+1)-\frac{W}{RT}\left(x^2+n(1-x)^2-\frac{n}{n+1}\right) \quad (1)$$

$$\ln(1-x)=-\frac{\Delta H_A}{RT}+\frac{\Delta H_A}{RT_A}-\frac{W}{RT}x^2 \quad (2)$$

$$\ln x=-\frac{\Delta H_B}{RT}+\frac{\Delta H_B}{RT_B}-\frac{W}{RT}(1-x)^2 \quad (3)$$

The adduct C is formed by one mole of A (guest) and n moles of *PHTP* (B, host); x is the mole fraction of B, and ΔH_C, ΔH_A, ΔH_B, T_C, T_A and T_B are the enthalpies and temperatures of melting of C, A and B, respectively.

Equations (2) and (3) correspond to the liquidus curves (van't Hoff equations) of pure A and B, respectively, which intersect the liquidus curve (Prigogine equation) of the adduct C at the eutectic points E_1 and E_2. The solidus temperatures T_{S1} and T_{S2} differ from that calculated from Eqs (2) and (3) for the metastable eutectic containing only A and B.

Deviation from ideality in the liquid state is accounted for by using the repulsive interaction parameter W, which is defined in the framework of regular solutions [18].

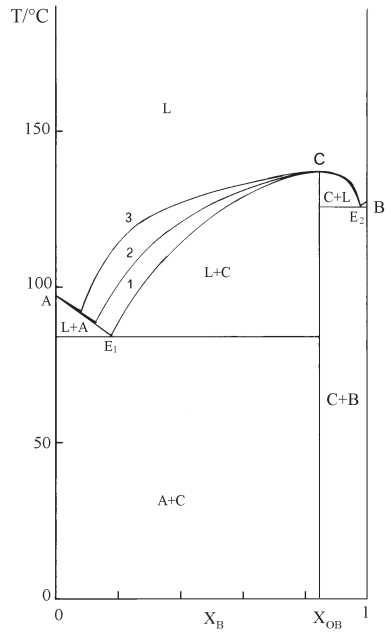

Fig. 2 Calculated phase diagrams of *PHTP* adducts. T_A, T_B, T_C, $\Delta H_A/R$, $\Delta H_B/R$, $\Delta H_C/R$ and n values: 370, 400, 410, 2000, 2900, 19000 K and 5.5. Curves 1–3 were calculated for W/R values of 0, 250 and 500 K, respectively

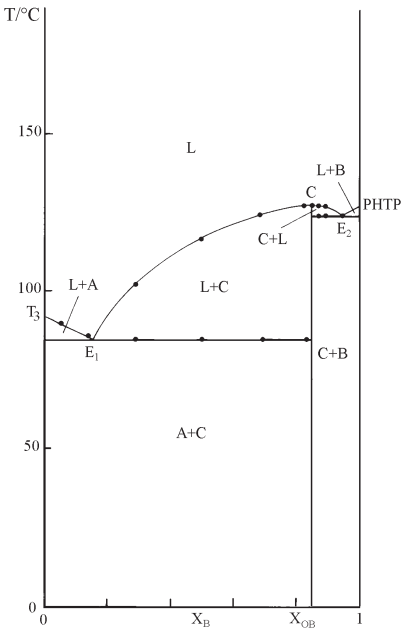

Fig. 3 Experimental phase diagram of *PHTP*/terthiophene mixtures (solid line: calculated)

In the case under study, the observed W value is not so high and curves can be described by unmodified equations (Fig. 2).

Figure 3 presents the complete phase diagram of *PHTP*/terthiophene mixtures. The reported curves were calculated by using T_A, T_B, T_C, $\Delta H_A/R$, $\Delta H_B/R$, $\Delta H_C/R$ and n

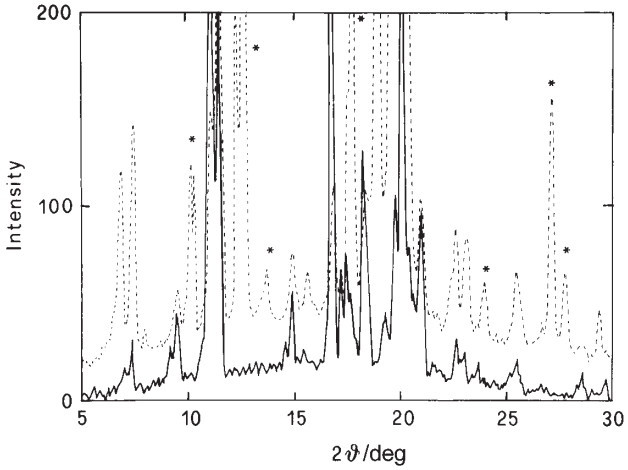

Fig. 4 X-ray diffraction patterns of *PHTP* (bottom) and of *PHTP/T3* adduct and *PHTP* mixture (top). Asterisks indicate main diffraction effects of the adduct

values: 364.65, 400.25, 400.55, 2759, 2924.06, 18944 K and 5.7. All these data were determined by means of DSC experiments; *n* was evaluated by considering the stoichiometry of the linear hydrocarbon possessing the same end-to-end distance. The best fitting of the experimental data was obtained for W/R=250 K.

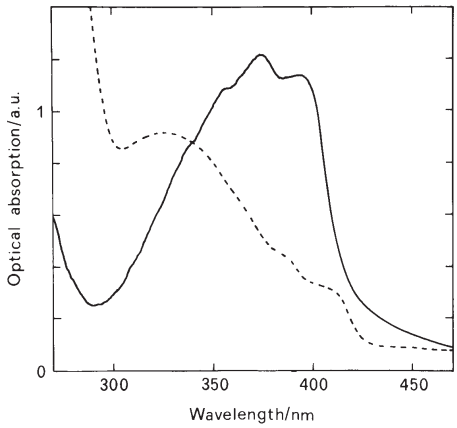

Fig. 5 Optical absorption of *T3* inclusion compound (solid line) and *T3* film (dashed line)

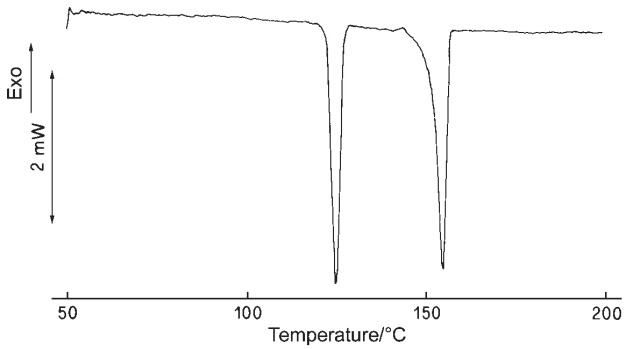

Fig. 6 DSC curve of a *PHTP*/*DH4T* mixture

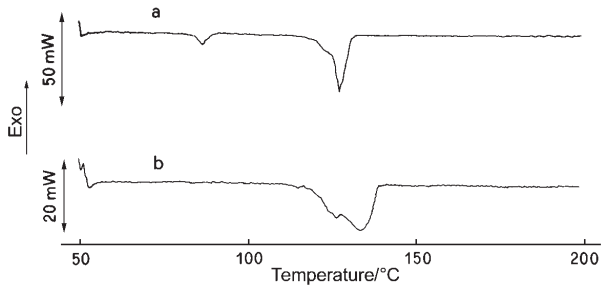

Fig. 7 DSC curve of a *PHTP*/(*T3*+*T5*) mixture (a – the first scanning; b – the second scanning)

Formation of an inclusion compound was confirmed by the X-ray data (Fig. 4) and by electronic absorption (Fig. 5). In [5], the X-ray powder spectrum of the *T3/PHTP* adduct was discussed, and pseudo-trigonal symmetry was inferred. The cell dimensions according to this model are: $a \approx b = 25.3$ Å, $c = 43$ Å, $\alpha = \beta \approx 90°$ and $\gamma \approx 120°$. Quite similar conclusions were reached by studying the *T5*/*PHTP* adduct.

For all the other thiophene oligomers, it was not possible to measure the complete phase diagrams, due to the high melting points of the guests. According to the DSC and optical results obtained for the *T3*/*PHTP* system, formation of the adduct is deduced from the presence of an exothermic peak after the *PHTP* melting point and from study of the optical spectra. Figure 6 demonstrates the presence of the adduct in a *PHTP*/*DH4T* mixture (x_{OB}=0.9). Analogous evidence arises in the *PHTP*/(*T4*+*T5*) systems (Fig. 7), where co-inclusion is observed.

Conclusions

A knowledge of phase diagrams in the presence of inclusion compounds is a very useful tool for interpretation of the optical properties of molecules used in non-linear optical studies. The optical properties of isolated π-systems can be studied, and differences with respect to the bulk or solution spectra are easily understood.

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Electronic absorption spectra were kindly run by Dr. C. Botta. *T4* was kindly supplied by G. Barbarella, and *T5* by S. Destri. The research was supported in part by CNR, Rome and MURST, Rome.

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