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PHASE DIAGRAMS OF PERHYDROTRIPHENYLENE AND AROMATIC COMPOUNDS

I. Trans stylbene and 4H-cyclopenta[2,1-b:3,4-b'] dithiophene

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Abstract

Perhydrotriphenylene (PHTP) forms channel-like adducts with molecules of different size and molecular weight. In the crystal structure of the adduct the included long sequences of molecules are separated from each other by the channel walls. The optical properties of the included molecules differ from those of the bulk molecules. The phase diagram of mixtures of PHTP and trans stylbene and 4H-cyclopenta [2,1-b:3,4-b'] dithiophene (CPDT) were determined by DSC experiments. Ideality in the liquid phase was observed only in the PHTP/CPDT system.

Keywords: perhydrotriphenylene, phase diagrams, *trans*-Stylbene inclusion compounds solvents

Introduction

Since its discovery perhydrotriphenylene has been a source for new fields of application. In fact Farina synthesised the anti,trans,anti,trans,anti,trans isomer [1] (I) as the cyclic model of some ditactic polymers [2]. The presence of a three-fold axis in the structure induces the formation of crystalline adducts [3] like that formed by urea or thiourea with linear hydrocarbon [4, 5]. In contrast to urea and thiourea, the solid phase of PHTP is stabilised only by very weak van der Waals interactions. As a consequence, PHTP forms inclusion compounds with guests of different size and polarity [6] without the selection phenomena observed in urea and thiourea where strong hydrogen bonds are present.

The polymerization of diene monomers included in PHTP is a topochemical reaction which transforms, by a radical mechanism, a long series of monomers inserted in channels, into macromolecules [7].

Polymers obtained by this method experience well defined conformational constraints during polymerization in the PHTP adducts and possess a pure 1,4-*trans* structure. When possible they are isotactic and can be used as standards

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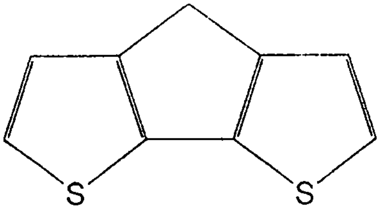
for NMR or other spectroscopic studies. The chains are in the *trans* conformation and each is isolated from the others. After purification from PHTP the polymers are free from impurities [8].

Recently the usefulness of PHTP as the ideal matrix for the study of UV spectra of isolated chains [9] and non-linear optical molecules was demonstrated [10].

The use of crystalline adduct as a matrix for polymerization, or as oriented phase of push-pull molecules, requires the knowledge of the phase diagram between the host and guest [11]. In this communication we present the phase diagram of some aromatic molecules and PHTP.

Materials and methods

PHTP was synthesised according to the literature [1]; the adduct with *n*-heptane was used for the 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 4H-cyclopentadithiophene was prepared according to the reference [12]. Trans Stylbene is a Fluka product and was used without further purification. DSC analyses were run on a Mettler TA 3000 apparatus. The Solidus Temperature (T_s) was measured at the peak temperature of the 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.



4H-cyclopenta[2,1-b;3,4-b']dithiophene (CPDT)

Results and discussion

Inclusion compounds can be described as binary compounds that undergo congruent or incongruent melting temperature and incongruent vaporisation. Crystalline adducts have been known for long time; they were discovered and discussed by Roozeboom [13] and van der Waals [14] at the end of the last century. The same thermodynamic relations work for gas hydrates [14], salt hydrates [14–16], complex metal halides [17] and semiconductors [18]. The analysis of the phase diagrams is reported in the classical book of Ricci [19]. In the organic field analogous systems are solvates but, in spite of their importance, no

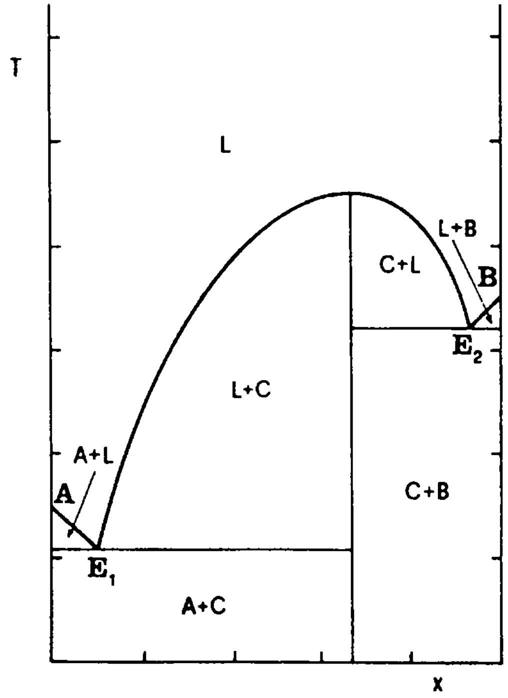


Fig. 1 Phase diagram of binary mixtures forming an adduct

systematic studies are reported in literature, the only exception being the case studied by Farina for inclusion polymerization [10].

The phase diagram of two molecules forming an adduct like an inclusion compound (Fig. 1) can be derived by overlapping two different phase diagrams, the first due to Guest (*A*) and Adduct (*C*) and the second due to *C* and the host molecule (*B*). The two diagrams overlap at the composition of the pure adduct. The resulting diagram is described by the van't Hoff [20] and Prigogine [21] equations (Eqs (1–3)) under the hypotheses: a) immiscibility in the solid phases, b) the adduct is present only in the solid state and c) ideality in the liquid phase [10].

$$\ln(1-x)+n\ln x=-\Delta H_C/RT+\Delta H_C/RT_C+n\ln n-(n+1)\ln(n+1) \quad (1)$$

$$\ln(1-x)=-\Delta H_A/RT+\Delta H_A/RT_A \quad (2)$$

$$\ln x=-\Delta H_B/RT+\Delta H_B/RT_B \quad (3)$$

The adduct *C* is formed by one mole of *A* (guest) and *n* moles of *B* (host); x is the molar 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 of the pure A and B respectively and intersect the Liquidus curve of the adduct C at the eutectic points E_1 and E_2. The T_{S1} and T_{S2} Solidus temperatures differ from that calculated from Eqs (2) and (3) for the eutectic containing only A and B.

Deviation from ideality in the liquid state can be accounted for by using the repulsive interaction parameter W which is defined in the framework of regular solutions (Eqs (4–6)) [22].

Equations (1–3) transform in Eqs (4–6):

$$\ln(1-x) + n\ln x = -\Delta H_C/RT + \Delta H_C/RT_C + n\ln n - (n+1)\ln(n+1) + \\ -(W/RT)(x^2 + n(1-x)^2 - (n/(n+1))) \qquad (4)$$

$$\ln(1-x) = -\Delta H_A/RT + \Delta H_A/RT_A - (W/RT)x^2 \qquad (5)$$

$$\ln x = -\Delta H_B/RT + \Delta H_B/RT_B - (W/RT)(1-x)^2 \qquad (6)$$

If the guest is a volatile compound, phase diagrams can be determined by tonometric measurements; reference 10 reports the corresponding equations.

Figure 2 presents the thermal curves of pure components CPDT, PHTP and *trans*-Stylbene. The corresponding molar enthalpies and melting temperature are: ΔH_{CPDT}=15.52 kJ mol^{-1}, ΔH_{PHTP}=20.84; T_{CPDT}=38.7°C, T_{PHTP}=125.7; ΔH_{TS}=30.9 kJ mol^{-1}, T_{TS}=122.3°C.

CPDT was polymerized by electrochemical oxidation and the electrical and spectral properties of the resulting conductive polymer were studied [12]. How-

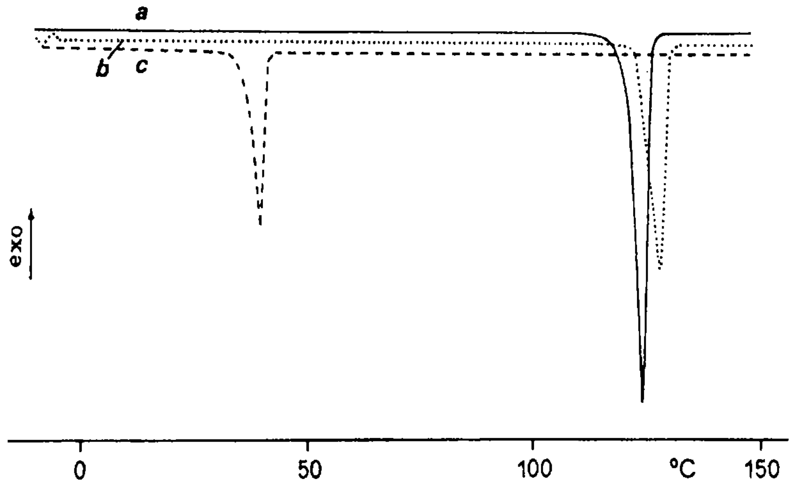


Fig. 2 DSC curves of pure: *trans*-Stylbene (a), PHTP (b) and CPDT (c)

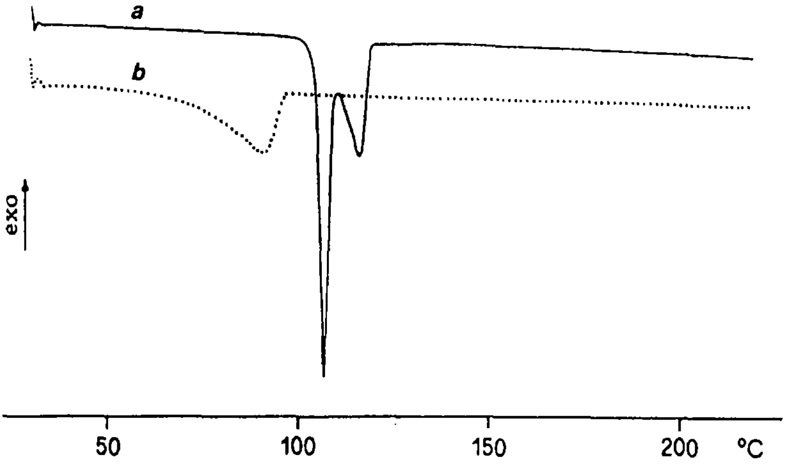


Fig. 3 DSC curves of PHTP/CPDT mixtures; a) x_B=0.95 and b) x_B=0.4

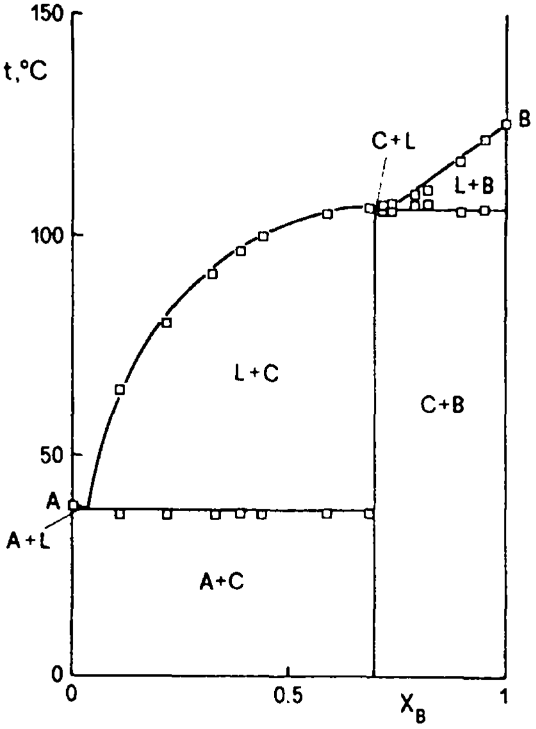


Fig. 4 Phase diagram of PHTP/CPDT system

PHTP

ever, in order to check the polymerization of CPDT by inclusion polymerization and produce a polymer free from ions, the phase diagram of the PHTP–CPDT is studied; in fact, inclusion polymerization requires the presence of the new solid phase of the adduct whose composition and stability are to be determined.

Figures 3 and 4 report some DSC and the phase diagram of PHTP/CPDT mixtures; the stoichiometry of the adduct was determined from the phase diagram and confirmed by the synthesis of the pure adduct (n=2.2525).

Ideal behaviour in the liquid phase is demonstrated by the coincidence of the theoretical Liquidus and Solidus Temperatures with the experimental ones for $W=0$, $\Delta H_C=67.3$ kJ mol^{-1} and $x_{OB}=0.6925$.

CPDT is the first polyaromatic molecule inserted into the PHTP crystal structure; *trans*-Stylbene can be considered the shortest polyunsaturated polymer with aromatic chain ends and a model for the study of the effect of the inclusion of polyacetylenes on their UV-Visible spectra. Work on this aspect is in progress.

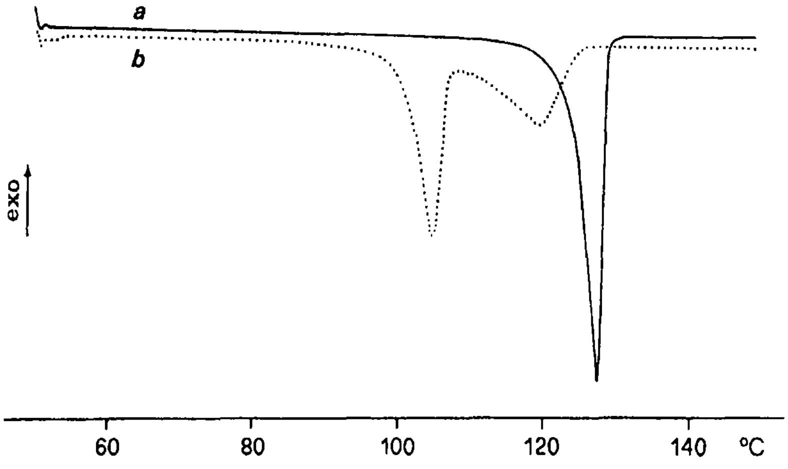


Fig. 5 DSC curves of PHTP/*trans*-Stylbene mixtures; a) $x_B=0.85$ and b) $x_B=0.6$

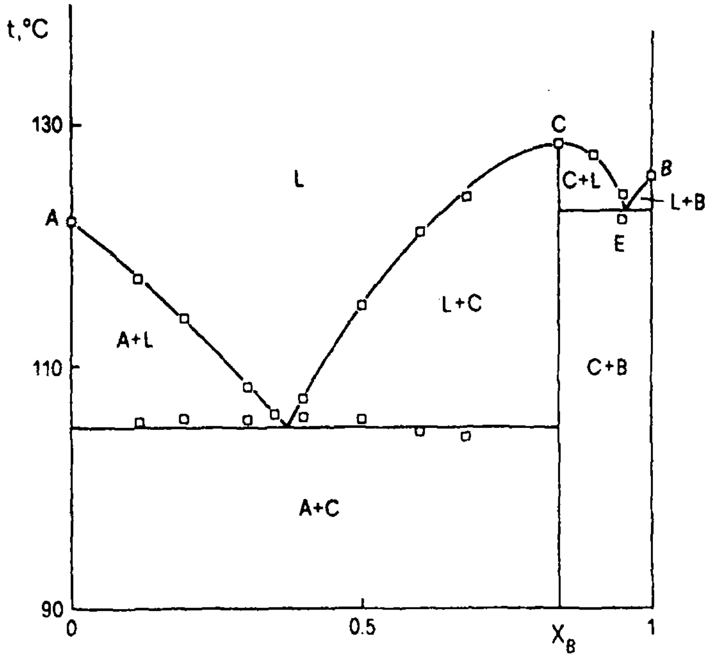


Fig. 6 Phase diagram of PHTP/*trans*-Stylbene mixtures

Figures 5 and 6 report two DSC curves and the T–x diagram of the *trans*-Stylbene-PHTP system.

As for CPDT, the stoichiometry of the adduct was derived directly from the T–x diagram and was confirmed by the synthesis of the pure adduct (x_{OB}= 0.841, n=5.289); the molecular weight of the adduct for one guest mole is 1481 g mol^{-1} and the corresponding ΔH_C is 140.7 kJ mol^{-1} guest.

In the PHTP/*trans*-Stylbene system the best agreement between the calculated and experimental Liquidus temperatures is observed for W=800 J; this fact suggests a quasi ideal behaviour in the liquid phase, according to the hydrocarbon nature of the host and of the guest, and is not longer different from that measured in PHTP/Dioxane mixtures.

Conclusions

In a previous work we demonstrated that oligomers of conducting polymers can be inserted in the channel of a PHTP/guest inclusion compound; in this paper we demonstrate the versatility of PHTP to include polyaromatic molecules whose behaviour is ideal or quasi ideal in thermodynamic and kinetic terms. In the case of the Thiophene oligomer (DPn=5) the high melting point of the guest (253.9°C) makes it difficult to determine the Liquidus points due to some decomposition. However, the formation of the adduct is confirmed by comparing the first and second scans of mixtures of PHTP and guest.

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