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Solvatochromism in poly[3-(10-hydroxydecyl)]thiophene: a spectrokinetic study of the conformational transition

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The solvatochromic conformational transformation of electroconductive poly[3-(10-hydroxydecyl)]thiophene in dimethylpropyleneurea solution, due to the addition of poor solvent, was investigated. A red shift of 80 nm in the ultraviolet–visible absorption maximum suggests a much more extended conjugated π-system for the new conformation. The time scale of this change allows a spectrokinetic analysis as a function of the type and amount of poor solvent. Second-order reaction kinetics are evident in all cases, and this is interpreted within the framework of an intrachain rearrangement leading to a higher coplanarity of thiophene rings in the new phase. A solid phase, laid down at very long times, gives insight about the final steps of an association process. Copyright © 1996 Elsevier Science Ltd.

(Keywords: solvatochromism; polyhydroxyalkylthiophene; u.v.–vis. spectrokinetics)

INTRODUCTION

Solvatochromism and thermochromism are special cases of order–disorder transformations of conjugated polymeric chains where strong couplings between the electronic structure and backbone conformations are operative. In this respect, substituted polythiophenes are very interesting because they show remarkable and rather complex solvatochromic and thermochromic behaviours, both in solution and in the solid state[1-5] as well as in the form of gel[6,7]. These phenomena depend on a number of factors such as, in the case of the solution, the kind of substitution, the solvent composition, and the reciprocal solubility of the solvents as a function of temperature. Two major factors[3] affecting the intramolecular potential and hence the backbone conformation have been pointed out both for solutions and the solid state: the steric hindrance of substituents and quantum needs for more extended electronic delocalization. Attractive intermolecular interactions should also play an important role in determining the skeletal shape. Steric hindrance should prevent the attainment of a planar arrangement of thiophene rings. Conversely, delocalization and attractive interchain interactions (solid state) could favour an extension of planar ring alignments. The transition is believed to occur when a reversible equilibrium between the two forms is set up and moderate changes in the operating parameters such as temperature or solvent are sufficient to push the system in one direction or the other. Limit situations of steric hindrance, i.e. very high or zero, should prevent any kind of transformation.

Since substituted polythiophenes are promising electroconductors, their solvatochromic and thermochromic properties make them interesting for further applications. On the other hand, a more thorough knowledge of the origin of these properties may help to complete the understanding of their electronic behaviour under a variety of external conditions. Reported in this paper are the results of a kinetic analysis of the solvatochromic conformational transformation of poly[3-(10-hydroxydecyl)]thiophene (PHDT, *Figure 1*) by ultraviolet–visible (u.v.–vis.) spectroscopy. To our knowledge, in the field of conjugated electroconductive polymers, to date kinetic experiments on solvatochromic transformations have been reported only for substituted polydiacetylenes[8].

Dimethylpropyleneurea (DMPU) solutions of PHDT, mixed with a number of poor solvents in various relative ratios, show a transformation between two general forms of the polymer, leading to a remarkable colour change from yellow (A form) to blue-violet (B form) with time. The transformation is also affected by temperature. DMPU is a very good solvent and its PHDT solutions seem to keep one of the two forms (the A form) in a stable state. Various behaviours are observed with

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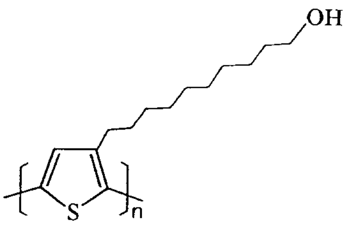

Figure 1 Poly[3-(10-hydroxydecyl)]thiophene

different poor solvents all able to promote the transformation. Similar behaviours are also observed when mixed solutions are submitted to heating. A detailed analysis has been made of the spectral changes by following the process spectrokinetically almost to completion. The kinetic order is discussed and a probable mechanism for the process is proposed.

EXPERIMENTAL

Poly[3-(10-hydroxydecyl)]thiophene was prepared by chemical polymerization of the monomer unit in a nitromethane/carbon tetrachloride solvent mixture using FeCl$_3$ as the oxidizing agent. Details of both the preparation method and the physico-chemical characterization of the material have been reported previously[9]. The polymer is insoluble in common organic solvents owing to hydrogen-bond interactions in the solid state, therefore molecular weight analysis could not be carried out.

Spectroquality or distilled solvents (those listed in *Table 1* and also chloroform), stored over molecular sieves, were used for the spectrokinetic measurements. Dimethylpropyleneurea (Fluka, >99%) was used as received. U.v.–vis. absorption spectra were recorded at room temperature (21°C) in 10 mm suprasil quartz cuvettes using a Varian Cary 05E UV-VIS-NIR spectrophotometer. Spectra at different temperatures, in the range 7 to 70°C, were obtained by fitting the sample compartment with a Perkin–Elmer spectrophotometric multicell block whose temperature was controlled externally by a Julabo VC circulator (±0.1°C). Temperature changes were made stepwise, allowing temperature stabilization at each step. For all kinetic experiments the polymer concentration was kept rigorously constant at 1.2×10^{-4} mol l^{-1} (moles of polymer repeat unit per litre).

For comparison, u.v.–vis. spectra of films of polymer cast from DMPU solutions on quartz plates were also recorded at room temperature, selecting the more suitable, homogeneous areas of the samples under a polarizing microscope (Leitz Orthoplan).

Kinetic procedure

In a cuvette the calculated amount of polymer solution in DMPU was added quantitatively with the calculated amount of poor solvent, so that two layers, miscible only by shaking, were formed. The cuvette was shaken rapidly and inserted in the sample compartment, starting the computer-aided measurements. An injection apparatus to mix the solvents was found to be unsatisfactory owing to the appearance of bubbles, so manual operations were preferred as the best procedure. Usually, at instrumental zero time, all experimental trends showed non-zero absorbances due to the sum of all time lags (up to 10 s) involved in the procedure. Thus, in our kinetic analysis, we shifted the absorbance forward along the time axis appropriately, so that zero absorbance corresponded to the true zero time. Four different wavelengths, i.e. 443, 521, 558 and 606 nm (2.80, 2.38, 2.22 and 2.05 eV), corresponding to maxima or shoulders of the spectral profile of the two forms, were tested for the measurements. The absorbance at 606 nm, exclusive to the B form, was assumed the more appropriate and proportional to the amount of the B form, so that increasing absorbances were monitored with time to follow the progress of the transition. Uncertainties about the actual structures of the chromophores led to the use of absorbance instead of concentration units in all kinetic calculations. The spectra of the samples were recorded, depending on the speed of the transformation, at least 120 min after the collection of kinetic data had stopped, i.e. when the absorbance became constant with time. The slower processes were followed at all the above wavelengths simultaneously by recording the absorbances cyclically every 30 s. With the faster processes, a single wavelength procedure was preferred to minimize the time lag.

RESULTS AND DISCUSSION

U.v.–vis. spectra

With the addition of a poor solvent, the u.v.–vis. spectral profile of a DMPU solution of poly[3-(10-hydroxydecyl)]thiophene changes with time at variable rate depending on the poor solvent itself (see example in *Figure 2*). In some special cases of a very high mole fraction (m.f.) of poor solvent, the change is so rapid that a scan speed of 400 nm s^{-1} fails to obtain reliable spectra during the transformation. In general, final spectral profiles appear as a mixture of two spectral systems, seemingly one for each form involved in the transformation. First, we tried to obtain spectra representative of each separate form. The spectrum of the pristine polymer in DMPU solution effectively seems to originate from a single phase (A form). As to a pure B form, traces of A form could not be excluded even at high dilution of suitable poor solvents. *Figure 3a* shows the spectrum of a pristine polymer solution (A form). It appears as a strong

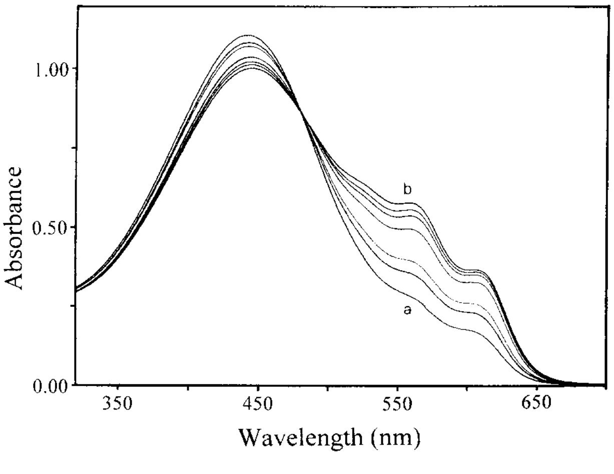

Figure 2 Development of PHDT spectral profile with time in DMPU/MeOH solution at MeOH m.f. = 0.6, recorded between (a) 20 s and (b) 185 min from the time of mixing

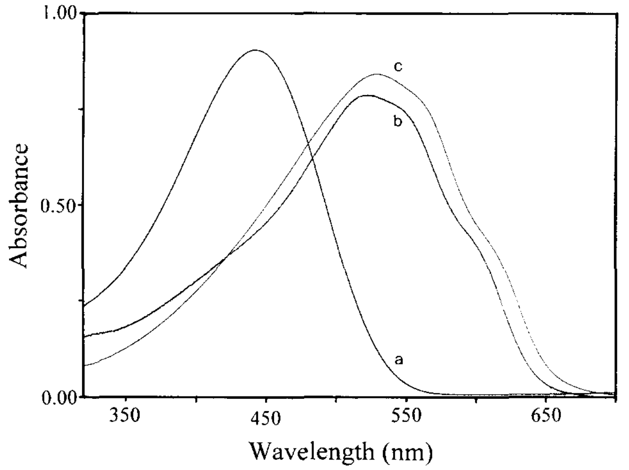

Figure 3 Absorption spectrum of PHDT in DMPU solution (a), 1 : 20 (v/v) DMPU/MeOH solution (b) and thin film cast from a DMPU solution (c)

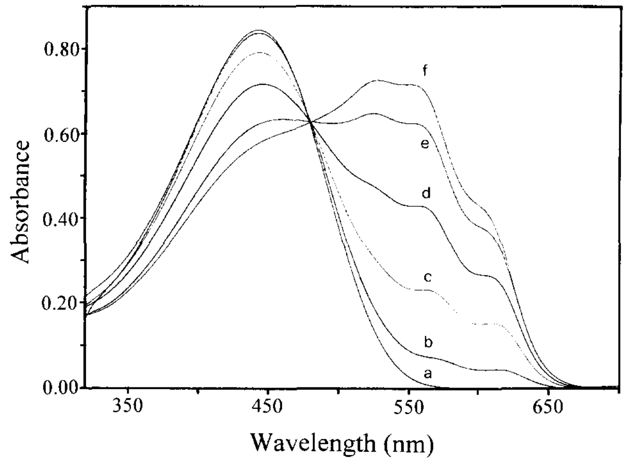

Figure 4 Absorption spectrum in DMPU/MeOH solution at different MeOH mole fractions: (a) 0; (b) 0.43; (c) 0.50; (d) 0.60; (e) 0.66; (f) 0.75

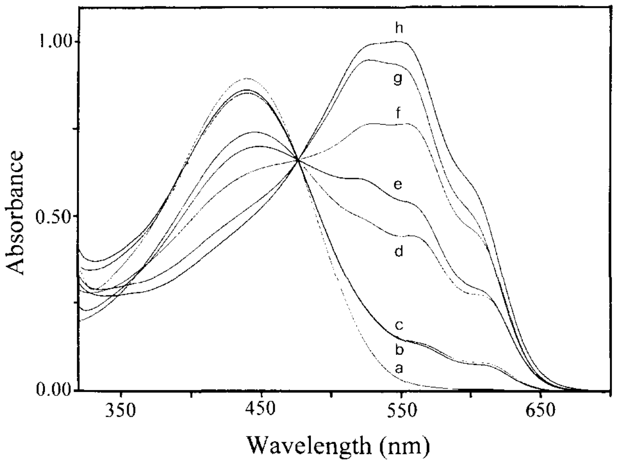

Figure 5 Absorption spectrum in DMPU/poor solvent solutions at m.f. = 0.60 of the poor solvent: (a) acetone; (b) 1-propanol; (c) 2-propanol; (d) methanol; (e) acetonitrile; (f) ethanolamine; (g) ethylene glycol; (h) water

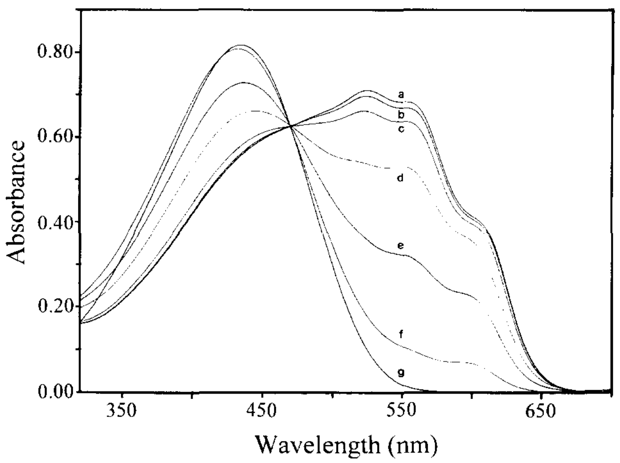

Figure 6 Absorption spectrum in DMPU/MeOH solution at MeOH m.f. = 0.75 at different temperatures (°C): (a) 7.5; (b) 8.0; (c) 17.0; (d) 41.6; (e) 54.0; (f) 70.2. The spectrum in DMPU solution at 21°C (g) is reported for comparison

asymmetric unstructured band located around 2.80 eV. *Figure 3b* shows the spectrum of a solution with a high relative amount of the B form, obtained in 1 : 20 (v/v) DMPU/MeOH mixture. Hereafter, this spectrum will be considered representative of the B form. It is structured, starting with well-defined shoulders at 2.05 and 2.22 eV and showing a maximum at 2.38 eV. The peaks and shoulders are separated by about 0.17 eV (1380–1360 cm^{-1}) and the spectrum can be interpreted as a vibronic progression starting from pure O–O electronic transitions of conjugated systems of limited extension on thiophenic chains. In polyalkylthiophenes a similar progression has been assigned to a C=C stretching mode strongly coupled to the electronic structure[1,10]. Assignments for different conformational phases have also been given[2,11], but we have evidence suggesting a vibronic structure of a single phase, which will appear in a forthcoming paper.

When increasing amounts of a poor solvent were added to a pristine polymer solution in DMPU with a rigorously constant polymer concentration, in our experiments 1.2×10^{-4} mol l^{-1}, mixed spectral profiles were obtained giving an apparent isosbestic point (see example in *Figure 4*); i.e. the addition pushes the transformation forward more and more. This fact confirms the existence of two distinct general phases. For the same DMPU solution, at constant concentration of the polymer, a similar isosbestic point is obtained when different types of poor solvent are added at fixed molar ratios with respect to DMPU (i.e. 0.6 mole fraction). The corresponding spectral profiles are shown in *Figure 5*, in which very different degrees of advancement can be observed. This reveals the different powers of the poor solvents in pushing forward the transformation. Conversely, when DMPU is added to solutions with a prevalent amount of the B form, the A form is recovered. Thus an apparent equilibrium between the two forms seems to be established, with a position that depends on the amount of poor solvent. Polymer solutions in mixed solvents submitted to a moderate heating process to about 70°C behave analogously (*Figure 6*).

Kinetic measurements

The direct process (A → B) implies a colour change with time and occurs over time scales suitable for spectrokinetic analysis. At relatively short times after the interruption of a kinetic run, no evidence was found

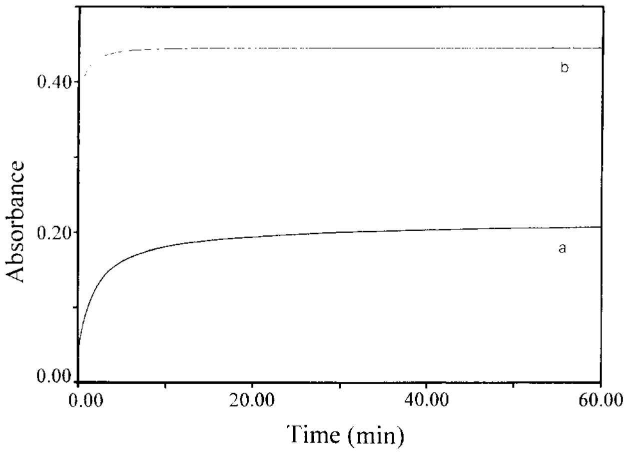

Figure 7 Time dependence of B form absorbance at 606 nm in DMPU/MeOH solution for MeOH mole fractions of 0.60 (a) and 0.75 (b)

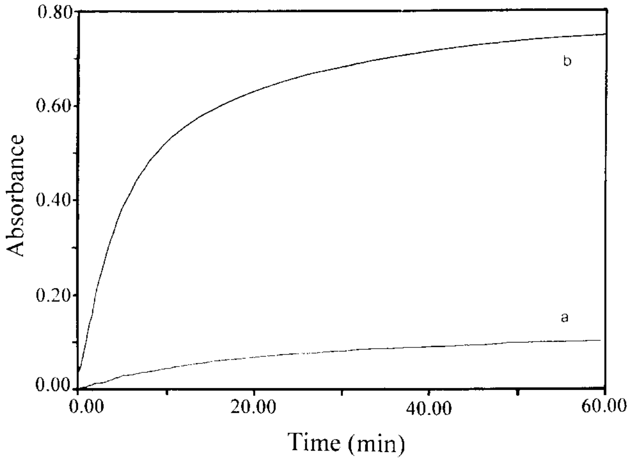

Figure 8 Time dependence of B form absorbance at 606 nm in DMPU/poor solvent solution at m.f. = 0.60 of poor solvent: (a) acetone; (b) 1-propanol

of any kind of solid phase. However, a solid phase appeared after longer times with larger amounts of poor solvents.

With methanol as the poor solvent, kinetic measurements were made within the range 0.40 to 0.75 mole fraction of methanol. Outside these limits the transformation was either extremely slow or too fast for our measurement system. An example of the general trend is shown in *Figure 7*. First we noted that the transformation reaction rate and also its degree of advancement are largely dependent on methanol mole fraction. It appears as if a threshold of m.f. = 0.40 has to be overcome before an appreciable reaction rate or amount of product can be detected. Then, within a relatively narrow m.f. range, the process starts with a rapidly increasing rate. Complete reaction is reached only at the upper limit of the range. Similar trends were observed (*Figure 8*) with the other poor solvents, together with drastically different reaction rates and with evidence of different thresholds and m.f. ranges. As for methanol, the transformations reached completion only at the upper limit of the ranges.

Kinetic orders and mechanism

To gain some information about the mechanism of the first steps of the process, equilibrium and non-equilibrium kinetic laws of different orders were investigated. It was found that a second-order kinetic law was followed consistently at all methanol mole fractions, as well as with all the other poor solvents. Almost invariant second-order rate constants k were observed for the entire process, and every attempt to fit first-order kinetic laws to the experimental data gave k values that changed unacceptably during each kinetic run. This point is discussed in more detail below.

An experimental second-order kinetic law is the classical basis for a bimolecular dominant step. We believe that this correspondence is valid here too, but it does not necessarily imply a chain–chain interaction process. Our experimental data rely on the absorbances of the chromophoric unit of the final B conformation, absorbances that are assumed to be proportional to its absolute concentration. Thus, a second-order kinetic law can imply a bimolecular process involving an interaction between chromophoric units of the initial A form and not necessarily between different polymeric chains of the same form (here, chromophoric unit means conjugated thiophenic chain-segments of different average length, one for each of the two A and B forms). For each kinetic law several models of the dominant single step, such as A + A = B or A + A = B + B and others, were assumed and tested. Only the first was found to be appropriate for a suitable description of the system. Examples of second-order characteristic quantities are plotted against time in *Figure 9* on the basis of the elementary second-order integrated equation for the direct process: i.e. $x/(a - x) = kat$, where a is the effective initial concentration of the A chromophore and x is the concentration of the B chromophore at time t. The measured rate constants k are collected in *Table 1*.

A nearly total transformation of the A form into the B form, mainly at higher molar fractions of poor-solvent, supports our intrachain hypothesis. If interchain association was the main event, it would be reasonable that some original conformations would remain unchanged, not being able to find around them a suitable segment of

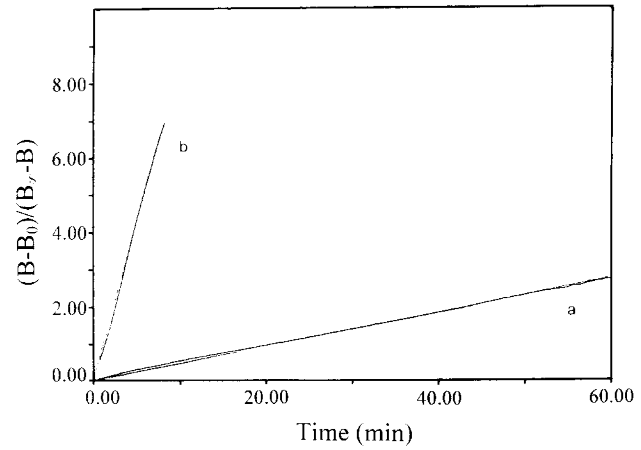

Figure 9 Experimental characteristic quantity $(B - B_0)/(B_\infty - B)$ for the direct second-order law *versus* time for DMPU/MeOH solution at m.f. = 0.60 (a) and m.f. = 0.75 (b) of MeOH, calculated according to $(B - B_0)/(B_\infty - B) \equiv x/(a - x) = kat$ where B, B_0 and B_∞ are absorbances of the B form at t, zero and infinite time. The best interpolated straight lines are also reported

Table 1 Second-order rate constants k and relative effective initial concentrations of the A chromophore in different DMPU/poor solvent mixtures

Poor solvent	Mole fraction	Rate constant $(\mathrm{abs}^{-1}\,\mathrm{min}^{-1})^a$ $A+A\rightarrow B$	$A+A\leftrightarrows B$	Effective initial concentration[b] (%)
Methanol	0.43	0.63(8)	0.63(6)	4.4
Methanol	0.50	0.75(1)	0.75(1)	22.4
Methanol	0.60	1.08(3)	1.08(2)	37.6
Methanol	0.66	6.72(2)	7.89(7)	66.6
Methanol	0.75	9.33(4)	10.98(5)	78.8
Water	0.60	1.76(0)	1.75(9)	100.0
Ethylene glycol	0.60	0.50(3)	0.50(3)	94.4
Ethanolamine	0.60	1.98(1)	1.97(8)	79.6
Acetonitrile	0.60	9.14(8)	9.13(7)	52.1
2-Propanol	0.60	0.83(1)	0.83(6)	16.1
1-Propanol	0.60	0.90(2)	0.90(1)	14.6
Acetone	0.60	1.48(5)	1.52(6)	2.5
1-Hexanol	0.60	2.07(3)	2.06(0)	1.7

[a] abs = absorbance

[b] Relative to the absorbance of the A chromophore in DMPU/water, taken as 100%

another chain to couple with appropriately in the final conformation. Considerable amounts of the original form would then always be evident in spectral profiles, and this is not the case. Difficulties connected both with chain diffusion lengths and times in solution, already emphasized for polydiacetylenes[8], are also against a direct identification of a bimolecular process with an interchain association. So, an intrachain process remains a unique candidate.

A more satisfactory transformation model, in agreement with experimental data and in better agreement with a bimolecular process, is an increasing intramolecular stiffening within each individual chain, where couples of adjacent segments, forced by a change in solvent properties, can interact and give rise to a new segment of more extended conjugation. The following experimental result support the proposed mechanism.

(1) The addition of different poor solvents, at constant m.f., to DMPU solutions pushes the transformation forward to different degrees. In a few cases the poor solvent induces total transformation into B chromophores, since there is no evidence of residual absorbance of the A form. Thus, the final absorbance of the B chromophores apparently reaches its maximum possible value. As a consequence, it could be reasonable to consider this absorbance as also being representative of the initial concentration of A chromophores.

(2) In all cases of partial transformation, however, the best fit of the experimental data with the proposed laws is obtained when the initial concentration of the A chromophore coincides with the final value of the B chromophore and not with its maximum possible value. The effective initial concentrations of A chromophores are found to be somewhat lower than their possible maximum value.

(3) When the effective initial concentrations arising from an ordinary second-order law are compared with those from direct second-order equilibrium laws (with first- and second-order reverse processes), one always finds the same values. Moreover, with these laws, very similar trends (such as those of *Figure 9*) are found.

The results provide the following indications. First of all, in each process, transformation progresses by consuming the amount of A chromophoric units available at the time, i.e. only the conjugated chain-segments made free for transformation, that are released from DMPU by way of a poor-solvent effect. Secondly, all three second-order laws mentioned above apply very well and a very high goodness of fit is obtained with all of them when the initial concentration of the A chromophore is assumed to be nearly identical to the particular final concentration of the B chromophore. This leads to the conclusion that a reverse process is always insignificant at all transformation stages. A reverse process is possible only by again increasing the DMPU percentage in the mixture. A simple ordinary second-order law, where the starting concentration of the A chromophore corresponds to only part of the total amount of polymer in DMPU, is thus applicable and an 'effective' initial concentration of the A chromophore corresponding to the effective amount of the A form involved in the transformation can be identified. The different degrees of advancement observed for the transformation would then follow not from the establishment of equilibrium from a kinetic point of view, but rather as a consequence of different degrees of release of chain-segments of the A form due to the effect of different poor solvents.

The following simplified model, therefore, can be proposed. When in solution in a very good solvent such as DMPU, the polymer chains, although in a fully unwound state, are imprisoned in solvent cages in forcedly twisted configurations (A form). This could imply a reduction in their average conjugation lengths with a consequent blue shift in the electronic spectrum. When a poor solvent miscible with DMPU is added, an interaction between the two solvents occurs, as suggested by the more or less evident evolution of heat. A reduction in the DMPU solvation efficiency, depending on the properties of the poor solvent and on its ratio to DMPU, could be expected. Thus, this new situation would allow mainly in-pairs segment–segment alignment and planarization with the establishment of longer conjugation lengths, together with a red shift in the electronic spectrum. A consequent more stable configuration (B form) could be achieved. The energy gain of the system, following the planarization, could be the main driving force of the transformation and, probably, also the formation of intramolecular hydrogen bonds can help overcome the energy barrier to the chain-segment planar alignment[12]. Very large blue and red-shifts (5200–5800 cm^{-1}) are observed when the system is forced in one direction or the other.

As a consequence of favourable encounters in solution, a diffusion-controlled interchain association process must necessarily follow. In this way, the formation of a solid phase, at much longer times and with completely different kinetic constants and mechanism, can be explained. The new B conformation generated could be a precursor to the order that is found in a thin film cast from a DMPU solution (*Figure 3c*).

Our hypothesis is outlined for methanol at 0.6 mole fraction, as an example, in the simplified *Scheme 1* where k is the rate constant.

The hypothesis that a couple of segments of the A form could interact giving a single segment of the B form is also supported by calculation of the conjugation

PHDT(A form)–DMPU + MeOH
(chain-segment release) ↓
PHDT(A form) ··· DMPU–MeOH
(chain-segment planarization) ↓ $k = 1.08\,\mathrm{abs}^{-1}\,\mathrm{min}^{-1}$
PHDT(B form) + DMPU–MeOH
(chain association) ↓
PHDT(solid) + DMPU–MeOH

Scheme 1

length. Two formulae were taken into account among the several reported that relate the conjugation length to the electronic absorption of a polyene system. The first, proposed theoretically by Khun[13,14] and parametrized for polyenes by Wenz *et al.*[15], relates the optical band gap (pure electronic transition) to the number of conjugated double bonds. The second, proposed semi-empirically by Jiang[16] and parametrized for polythiophenes by Cao *et al.*[17], implies the absorption maximum instead of the pure electronic transition. For the B form, 15 conjugated thiophenic units were calculated using the first formula (pure electronic transition at 606 nm) and 14 using the second (absorption maximum at 521 nm). For the A form, Jiang's formula gave six or seven thiophenic units for the absorption maximum at 443 nm. The pure electronic transition of the A chromophore was not well identified; however, an approximate calculation using the first formula gave a number of five or six. On the other hand, a comparison with u.v. absorptions of thiophene oligomers[18] gave, for the A form, an average length of seven thiophenic units.

Solvent effect on the transformation

Table 1 shows considerably different k values for the transformation for different DMPU/MeOH ratios. This fact led us to the hypothesis that all the measured values of k may actually be of a pseudo-second order type. The values could be products of an ideal second order k_i with another kinetic coefficient k_s accounting for each DMPU/MeOH mixture: $k = k_i \times k_s$. Perhaps the main quantity on which attention should be focused is k_s; however, at the moment, we cannot know its genesis and specific role.

From the kinetic results it follows that the effective initial concentration of the A chromophore (i.e. the effective amount of A form involved in the transformation) and the specific rate constant k of the transformation are completely independent parameters. The first parameter involves the solvation efficiency of DMPU, to which the release of A chromophore seems to be linked, while the second implies the effect of the medium on the transformation kinetics by way of k_s. If the effective initial concentration obtained by the addition of water is taken as a maximum (*Table 1*), it can be observed that for somewhat lower concentrations relative to other poor solvents much greater k values are found. For example, in the case of acetonitrile for an effective initial concentration of about one-half with respect to water, the k value found is five times greater.

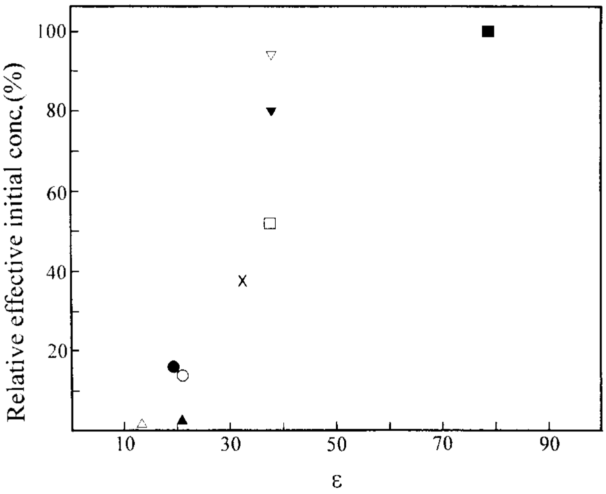

Figure 10 Dependence of the effective initial concentration of the A form on the dielectric constant ϵ (25°C) of poor solvents at m.f. = 0.60 in DMPU/poor solvent mixtures. Poor solvent: (△) 1-hexanol; (▲) acetone; (○) 1-propanol; (●) 2-propanol; (×) methanol; (□) acetonitrile (ϵ at 20°C); (▼) ethanolamine; (▽) ethylene glycol; (■) water. For ϵ values see refs 19 and 20

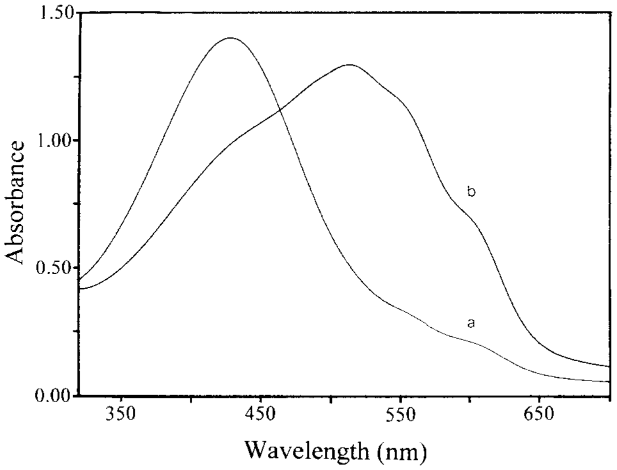

Figure 11 Absorption spectrum of PHDT in chloroform (a) and 1-propanol (b)

The effective initial concentration roughly increases with increasing dielectric constant ϵ of the solvent[19,20]. A general trend for all poor solvents at constant m.f. = 0.60 is shown in *Figure 10*. It can be observed that bifunctional poor solvents, able to form hydrogen bonds, are very efficient in making chain-segments available for the transformation. As far as monofunctional alcohols are concerned, a dependence on the alkyl chain length is also observed.

Some other qualitative information on the solvent effect comes from a comparison of the u.v.–vis. spectrum of PHDT in DMPU with those obtained in pure chloroform and 1-propanol solutions. With these poor solvents the solubility was accomplished only at spectroscopy level. A different state of entanglement of the alkyl side-chains, which induces variations in conformation and conjugation length of the polymer main chain, has been suggested as a possible explanation for the colour changes of polyalkylthiophene solutions in pure solvents[21]. From *Figure 11* it is evident that two clearly distinct forms (A and B type) are present in chloroform and 1-propanol. It appears as if an increasing percentage of one form springs up in the other form when a change in the properties of the pure solvent is made, while no evidence of a continuity of conformations between them is found. This fact agrees well with the scheme based on the kinetic results, which imply a change between two clearly distinct conformations.

Final observations on aggregation kinetics

The polymer chains, after transformation into the B form, seem to undergo a progressive aggregation until a particular solid phase is laid down. This phase is especially evident with the poor solvents that give a high concentration of the B form such as, for example, the 2 : 1 (v/v) DMPU/H_2O mixture (water m.f. = 0.77). In general this process is slow, its speed depending on the nature of the poor solvent. The new phase has an extremely soft consistency, its structure showing a very large prevalence of empty spaces. Nevertheless, it gives rise to a reticulated and elastic continuum which extends to the entire volume of the sample: a cluster apparently filling the whole container appears. Its stability is very poor. Extremely weak mechanical agitation dissolves it completely and some time is required to restore it again. Mechanical shaking brings back the coagulation process only for the B form, the A form being recovered only by heating at relatively higher temperatures or adding DMPU.

Indeed, different energies seem to be involved in each step of the entire process. Initially, an energy release is implied due to the following events: (1) DMPU–poor solvent interactions; (2) thiophenic rings twisting towards higher planarity of the chains; (3) extension of the conjugation over longer chain-segments. In fact, the addition of a poor solvent to pristine DMPU solutions is immediately followed by the evolution of heat. After these initial stages a very slow chain association process seems to start until the appearance of a condensed phase. This latter stage seems to involve much lower amounts of energy, with very weak bond formation at nearly every interchain encounter. This behaviour can be explained as an evolution of the B form towards a progressive interchain association that in some cases results in the formation of a kind of gel, a network usually showing elastic properties such as those observed by us.

CONCLUSION

A transition from the twisted to the planar conformation for PHDT in DMPU solution is found as the result of an intramolecular rearrangement when poor solvent is added. A dramatic blue shift of the optical absorption is linked to the conformational transformation of the polymer backbone. U.v.–vis. spectrokinetic analysis suggests second-order reaction kinetics involving adjacent chain-segments, whose interaction leads to a longer conjugation length.

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