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Conformational Transformations in Chiral Polythiophene Derivatives Aggregated in Polymethacrylate Matrices: Experiments and Molecular Dynamics Simulations

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Abstract: Chiral derivatives of poly(3-(S-3',7'-dimethyloctyl)thiophene) embedded in either poly(methyl methacrylate) (PMMA) or poly(butyl methacrylate) (PBMA) were studied by polarization optical microscopy, UV absorption and circular dichroism (CD) spectroscopy as well as simulated using the Molecular Dynamics procedure. CD spectra change on heating to mirror spectra; for PMMA-containing blends the changes in heating/cooling cycles are reversible. The signs of CD spectra depend on free volume, the packing of side groups in particular. Since in the melt there are no restrictions on the positions of the chiral groups, those groups appears with equal probabilities at any locations with respect to the thiophene ring. By contrast, in clusters restrictions imposed by other alkyl chains result in positioning of chiral methyl groups preferentially on the left or right sides of the thiophene rings. The consequence is the formation of right or left twists in molecular backbones.

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1. Introduction

Derivatives of polythiophene (PT) are promising components of electro-optical devices [1, 2)]. Chiral PTs are potential sensors – provided they can undergo large changes in their conformations. Such changes might be induced by temperature or else by solvent quality variations, thus providing temperature and/or chemical sensors.

Substituted chiral polythiophenes have been obtained by several research teams [3 - 6)]. For instance, Guillerez and coworkers [3)] have synthesised PTs with a chiral assymetric atom introduced into pendant alkyl groups as an internal probe, thus inducing chirality in the polymer backbone.

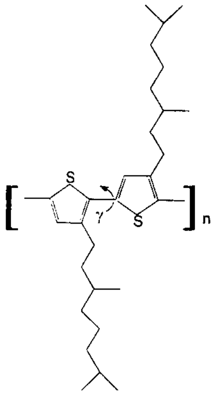
We consider the solvatochromic effect, that is changes in color induced by changes in solvent properties. Solvatochromic transitions in chiral PTs were shown to be accompanied by the formation of aggregates with S- or R- chiral structures of the backbone [3)]. In the case of a (S-) chiral atom in a pendant group, an abrupt formation of a R- aggregate was revealed by varying the solvent quality from good to poor. The structure of the resulting aggregates was unresolved.

Other types of chiral polythiophenes have been synthesised by Meijer e.a. [4)] using a method developed by McCullough [5)]. The solid state thermochromism of this polymer is typical for PTs - except that a mirror image circular dichroism (CD) spectrum is observed when the polymer is cooled very fast from a high temperature unstructured state. No chirality in the backbone has been observed at the melting point. The effect was thought to be driven by an aggregation effect and was found to be reversible. The same effect were also found in poly (3,4 di(S) 2 methylbutoxy-thiophene) synthesised by Langeveld-Voes e.a [6)] and studied using CD as well as circular polarized luminescence. In spite of the effort expended, mechanisms of chiral transitions are still under discussion.

From the standpoint of the applications of chiral PTs, their blends with other polymers appear promising. Such blends might lead to flexible polymer films with varying chirality. As noted in the beginning, the variations can be induced by temperature and also by environment changes. A survey of the literature, however, shows that there are several papers on thermochromic and solvatochromic transitions in non-chiral polythiophenes 7). There is a lack of experimental and theoretical information on conformations and structures of chiral derivatives of polythiophenes and their aggregates inside polymer matrices.

While there is a large variety of candidate polymer matrices, we have chosen methacrylic polymers and their copolymers. In this case, the matrix and alkyl substituted polythiophenes have similar chemical structures of side chains so that compatibility is expected.

The aim of the present work is experimental and theoretical study of conformations of a regioregular chiral polythiophene, namely poly(3-(S-3',7'-dimethyloctyl)thiophene) (CHPT) in polymer matrices based on methacrylic polymers and the role of aggregation of CHPT macromolecules in the chiral properties of its blends. The chemical structure of CHPT can be represented as



2. Experimental

The chiral polythiophenes were prepared by the method described by Bidan and coworkers 3). Poly(methyl methacrylate) (PMMA) and poly(butyl methacrylate) (PBMA), each with the weight-average molecular mass of $M_w \approx 4.5 \cdot 10^5$ were used as matrices. The polydispersity index $M_n/M_w \approx 3$, where M_n is the number-average molecular mass. The methacrylates were obtained from PolyScience, USA.

Blends of CHPT in turn with PMMA and PBMA were prepared in the form of films by mixing the components in solutions of chloroform followed by casting on glass substrates and evaporation of the solvent.

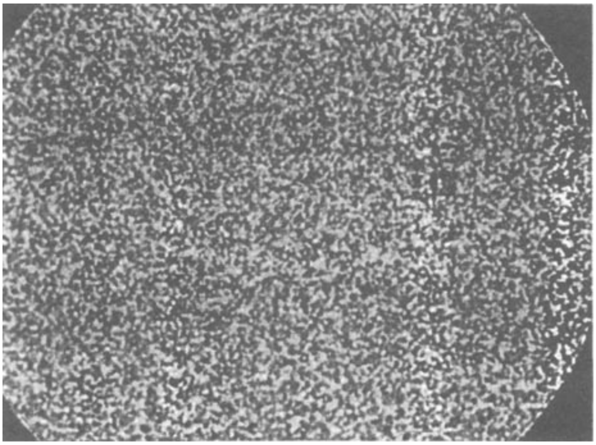
Polarization optical microscopy was used to study phase structures of the blends. Thermochromic transitions were determined using a Hitachi spectrophotometer equipped with a Mettler FP-82 hot stage.

CD spectra were recordered by using a Jasco spectrophotometer from Japan. Phase changes were determined with a Perkin-Elmer Differential Scanning Calorimeter (DSC-7).

3. Optical Microscopy

We have varied the CHTP concentration in the blends, starting from low CHTP contents. In all blends visible crystallites of CHPT appear in the polymer matrix at CHPT concentrations exceeding 1 weight % . We have observed that the matrices themselves are slightly colored; the coloring may be related to the presence of molecular level dispersion of CHPT.

Photographs obtained with the microscope are shown in Fig. 1 for both matrices, in each case for the concentration of CHPT of ≈ 1.2 wt. %. It is evident that the aggregates of CHPT are larger in the PMMA matrix than in the PBMA matrix.



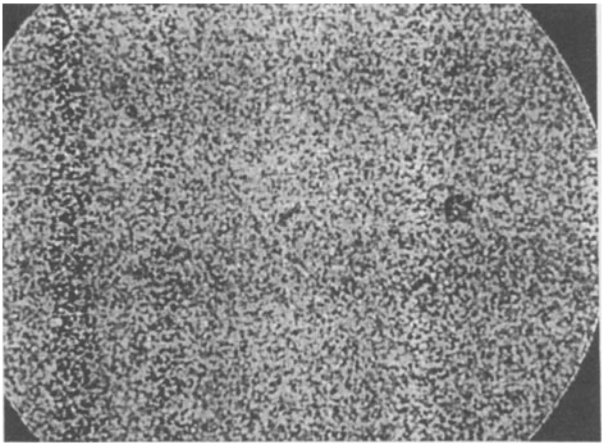


Fig. 1. Polarized optical microscopy photographs: PMMA + CHTP blends (previous page) and PBMA + CHTP blends (this page), each with the CHTP concentration of ≈ 1.2 wt. %.

4. Differential Scanning Calorimetry

DSC runs were made on films removed from glass plates and placed in aluminium pans. Results obtained in second heat runs are displayed in Fig. 2 for pure CHTP and also for the PMMA + CHPT blend containing 30 wt. % CHTP. Incidentally, the differences between the first and the second heat runs are insignificant.

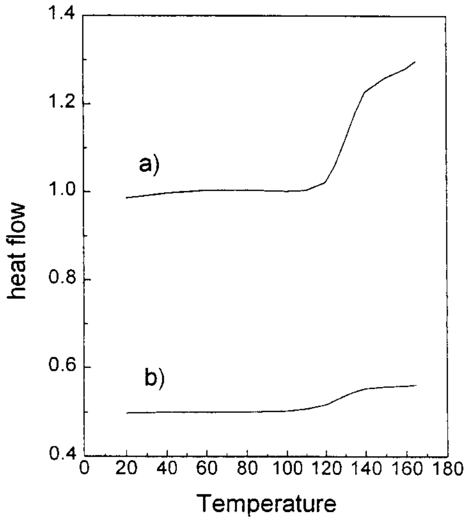


Fig. 2. DSC second heat runs for a) pure CHPT and b) for the PMMA + CHPT blend with 30 wt. % CHPT.

CHPT is initially in glassy state, up to the clearly visible glass transition around 135°C. As for the blend with PMMA represented by curve b), we see that the glass transition begins near 122°C. In PBMA blends containing 30 wt. % of CHPT a separate glass transition of the latter is not easily discerned. We recall that the microscopy has shown us finer dispersion of CHPT with PBMA than with PMMA. We have found that at lower concentrations of CHPT the DSC results do not show separate glass transitions of CHPT. Apparently we are then inside of the solubility limits of CHPT in the two methacrylates.

5. Circular Dichroism

Here again one used films obtained by casting from chloroform solutions. The CD spectra for pure CHPT at several temperatures are shown in Fig. 3.

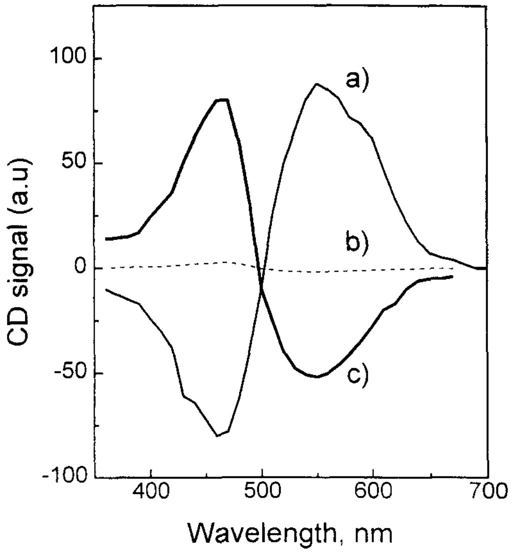


Fig. 3. Circular dichroism spectra of pure CHTP at several temperatures: a) 30°C; b) 120°C; c) after cooling back to 30°C .

We see in Fig. 3 that increasing the temperature leads to virtual disappearance of the signal at 120°C. Cooling from the melt back to 30°C results in the appearance of the mirror image of the original CD spectrum. Thus, the transitions are not reversible; neither other heating/cooling cycles nor variation of the rates of cooling lead us back to the initial spectrum.

In Fig. 4 we show results for ≈ 0.9 wt. % CHPT in the PBMA matrix. A vastly different behavior than that seen in Fig. 3 is now observed.

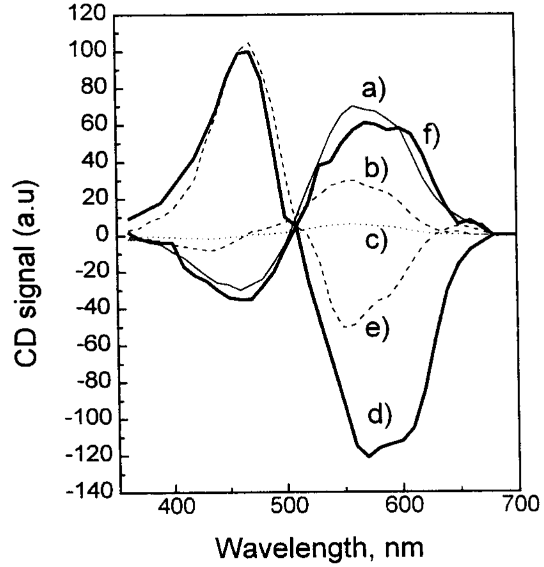


Fig. 4. CD spectra of 0.9 wt. % CHPT in the PMMA matrix: a) 30°C; b) first heating to 70°C; c) first heating to 120°C; d) first cooling to 30°C; e) second heating to 80°C; f) second cooling to 30°C.

There is no appearance of a mirror image under the cooling from 130° C in Fig. 4. Similar experiments for blends with concentrations of CHPT higher than 4 % show that the behavior is the same as in pure CHPT; the inverse CD spectrum appears under the cooling from melted state. Thus, the CD spectra are similar to those for pure CHPT. Here also transitions from mirror CD spectra to initial spectra could not be obtained by varying the rate of cooling or heating nor by quenching from a different temperature. As expected, the most significant differences in aggregate distributions are reflected in CD spectra recordered at different temperatures.

In PMMA matrices the mirror images are not observed for concentrations of CHPT lower than 0.2 wt. %. For ≈ 0.8 wt. % the effect is seen clearly and becomes reversible. We were able to achieve up to four transitions between initial and mirror states in heating/cooling cycles. We have shown in Fig. 4 only two transitions since all of them look alike. At higher CHPT concentrations the number of reversible transitions seems to decrease; they disappear entirely at ≈ 10 %. Nevertheless, the single transitions in films casted from chloroform remains.

6. UV Spectroscopy

Thermochromic transitions accompanying the chiral transitions were studied in more detail by UV spectroscopy. In Fig. 5 we show the results for 3.0 wt. % CHTP in the PMMA matrix.

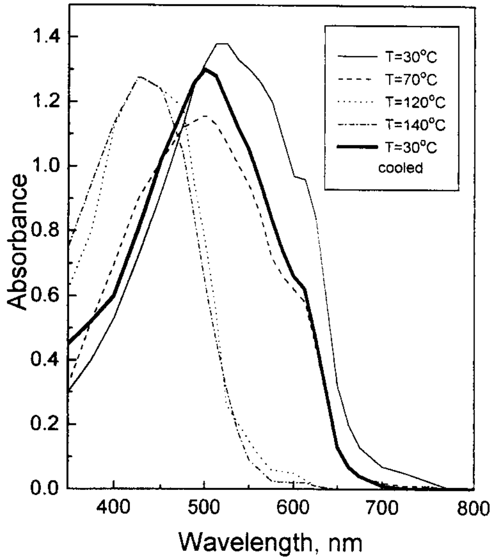


Fig. 5. UV absorbtion spectra of PMMA + 3.0 wt. % CHPT at several temperatures.

We observe, first of all, that the UV spectra are quite similar to those observed for non-chiral regioregular alkyl thiophenes [7]. At 30°C the spectrum is characterized by a typical vibrational fine structure in the 450-650 nm region, with the peaks at approximately 609 nm, 565 nm, 525 nm and 480 nm, with the highest peak at ≈ 525 nm. Increasing temperature results in the shift of the highest peak towards shorter wavelengths. Furthermore, as a result of heating, intensity of the peaks at 609 nm and 525 nm decreases, whereas the intensity of the short wavelength peaks increases. At 140° C, the fine vibrational structure degenerates and only the band at 440 nm is observed. There is - although not well-pronounced – an isosbestic point at 470 nm which suggests the coexistence of two phases in our blends.

For the PBMA + CHPT films, again with 3 wt. % CHPT, the corresponding spectra are shown in Fig. 6. We observe that the relative intensities of the peaks as well as their positions are very close to those found for PMMA + CHPT. As temperature increases, the changes in spectra are similar to those for pure CHPT film. The isosbestic point is clearly seen. However, in the PBMA matrix the degeneration of the fine vibrational structure takes place at a lower temperature, namely at 110°C. That difference may be explained also in terms of smaller sizes of CHPT aggregates in the PBMA matrix.

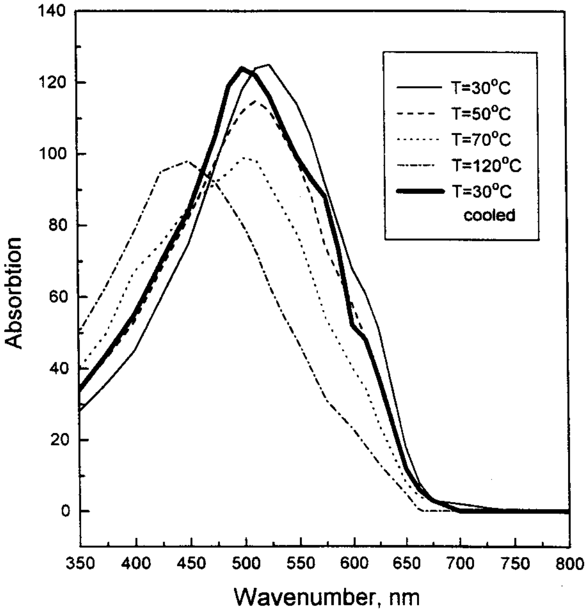


Fig. 6. UV absorbtion spectra of PMMA + 3 wt. % CHPT blends at several temperatures.

The formation of smaller crystalline aggregates is favored by the interaction between side chains of CHPT and pendant groups of the host polymer. Moreover, in the temperature range we have investigated, PBMA is above its gl;ass transition, hence necessarily it has higher free volume than glassy PMMA (at $T < 100^\circ$ C). We recall that the free volume is defined by

$$v = v^* + v^f \qquad (1)$$

Here v is the specific volume, for instance in cm^3g^{-1}, v^* the characteristic ("hard core", "incompressible") volume and v^f the free volume, all three in the same units. The importance of v^f for thermophysical properties of polymeric and other systems has been conclusively demonstrated by Flory and his students [8-12)]. In the present case high average v^f in the PBMA + CHPT system enhances the mutual solubility of the components.

Given the last conclusion, let us return briefly to the CD results. Decreasing the size of CHPT aggregates results in an increase of the fraction of CHPT molecules located at the cluster surface as compared to those inside the cluster. Necessarily, the surface molecules are more influenced by the polymer matrix than those inside the cluster. This is why the CD spectra of PBMA + CHPT blends do not change in heating/cooling cycles at concentrations of CHPT up to 4 wt. %, whereas the mirror image appears in the spectra of PMMA + CHPT blends already at 0.8 wt. % CHPT. We find that the average free volume v^f in the blend influences conformational and electronic properties of individual CHPT molecules. Since the free volume in the PBMA-containing blends is higher than in the PMMA-containing ones, in the former we have more conformational transitions of CHPT molecules at the cluster surfaces. This beyond the already discussed effects of the matrices on the sizes of the CHPT aggregates.

7. Molecular Dynamics Simulations

To better understand coreelations between conformational changes in CHPT molecules and experimental results reported above, we have also performed molecular dynamics (MD) computer simulations. The MD procedure has been developed by Metropolis and

Ulam already in 1949 13) ; apparently they have anticipated computer speeds much higher than they had available at that time. The technique has been used since in a variety of disciplines, including simulations of polymeric materials subjected to mechanical forces 14 - 16) . A review of MD simulations has been provided by Klein 17) and also by one of us 18) .

Simulation of molecular dynamics were performed using software called BIOSYM/MSI and Discover-3 package 19). Initial chemical structure of macromolecules were generated by combining chemical groups into molecules using standard bond lengths and angles, followed by minimizing the total energy of each molecule in vacuum. We have used that package together with a Consistent Valence Forcefield (CVFF). The field parameters used by us are the same as those of Dauber-Osguthorpe and coworkers 20).

The following terms were considered in the CVFF forcefield:

i) diagonal terms representing the energy of deformation of bond lengths, bond angles, torsion angles and out of plane interactions in a molecule;
ii) off-diagonal terms representing couplings between deformations of internal coordinates; and
iii) non-bonding terms reflecting interactions of atoms unconnected by chemical bonds, thus including van der Waals dispersive forces.

The simulations were performed (a) for a single CHPT macromolecule in vacuum and (b) for the system based on one cluster of three parallel CHPT molecules. The atom-atom summation method of van der Waals interactions was used together with the cutoff distance of 1.2 nm. The choice of that cutoff distance allows the inclusion of attractive intermolecular energy acting on the solute CHPT molecule with a reasonable accuracy (more than 75 % of the van der Waals interactions). A higher cutoff distance would lengthen the computation time without affecting our conclusions.

Single molecule simulations in vacuum were performed in order to search for possible chirality in the CHPT backbone in a good organic solvent - or in a polymeric matrix such as PBMA. MD runs for four initial conformers consisting of twenty monomers were performed. After total energy minimization, the system was equilibrated for 300 ps and then kept at 450 K for 950 ps. Chang and Freed [21] have shown that ≈ 1 ns is sufficient to span the conformational space and to elucidate the existence of intramolecular correlations. The attractive part of interatomic interactions was eliminated in order to simulate the situation in a good solvent. A justification for this approach has been provided by Grosberg and Khokhlov [22]) and the approach has been used by some of us before [23]). The probability distribution function for finding a molecule in a conformation state defined by the dihedral angle γ and calculated this way is shown in Fig. 7.

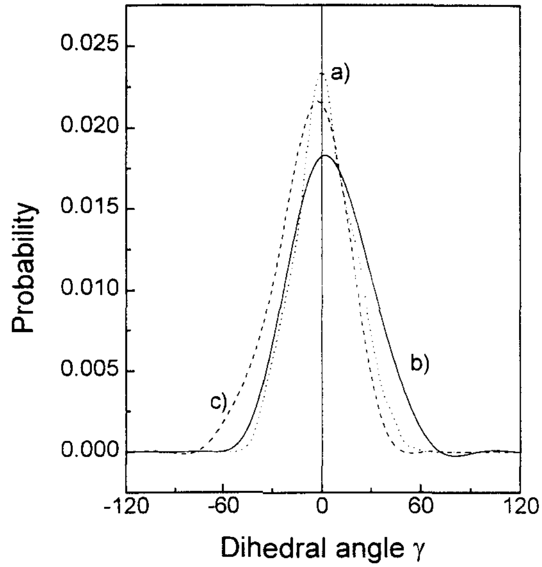


Fig. 7. Distribution of dihedral angles in the backbone: a) a single CHPT molecule; a cluster with the average initial distance between molecules equal to 0.38 nm; c) ; a cluster with the average initial distance between molecules equal to 0.50 nm

Inspecting Fig. 7 we see that the distribution of dihedral angles between thiophene units has a half-height width of ≈ 35°. This reflects the situation of the CHPT molecule in a good organic solvent – and presumably also in PBMA at low concentrations.

In the case of simulation of a cluster of CHPT molecules, the initial structure of the cluster was prepared by placing three molecules in such a way that their backbones were parallel to each other. Then the total energy of the cluster was minimized. During first 300 ps the system was equilibrated by running dynamics and kept at constant temperature and volume for 650 ps. The total time used for the MD simulation was 950 ps. The conformations of molecules were collected during the last 650 ps. Each conformation was picked up after 120 fs and averaged over four neighboring conformations. In order to span the conformational space efficiently, here also the system was kept at the temperature of 450 K.

The results of the cluster simulations are seen in curves b and c in Fig. 7. All molecular backbones have twisted structures. The distribution of dihedral angles is not symmetric, with the excess of either right or left isomers. Nevertheless, *over the whole cluster* the distribution of dihedral angles is found to be symmetric. Thus, the cluster should not provide any contribution to CD spectra. A more detailed analysis of molecular conformations shows that the distribution of dihedral angles determining orientation of chiral methyl group is different for molecules with right and left backbone spiral: for molecules with right backbone spiral there is excess of conformers with $\gamma = +60°$ while for molecules with left backbone spiral there is excess of conformers with $\gamma = -60°$.

8. Concluding remarks

Experimentally we have found reversible changes in the CD spectra of PPMA + CHPT blends. We infer from the MD simulations that the direction of the twist induced in the backbone of chiral polythiophene is related to the position of the chiral methyl group with respect to the plane of thiophene rings. In the melt, with no restriction on the positions of the chiral group, that group has to appear with equal probabilities at any side of the thiophene ring. In clusters there are some restrictions imposed by neighboring molecules, particularly other alkyl chains, that results in positioning of chiral methyl groups preferentially on the left or right sides of the thiophene rings. It is this situation which causes the formation of right or left twists in molecular backbones. We conclude that the amount of free volume v^f available and the resulting molecular packing determine the formation – or otherwise – of chiral structures.

Acknowledgments

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