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CHIROPTICAL PROPERTIES OF REGIOREGULAR CHIRAL POLYTHIOPHENES

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Abstract The synthesis and (chir)optical properties of a highly regioregular optically active 3-substituted polythiophene are reported. Using the McCullough method a regioselectivity of more than 98% is found for the head-to-tail coupling in 3-[2-((S)-2-methylbutoxy)ethyl]polythiophene **1**. Contrary to the small effects observed for the regiorandom analogue **2**, made by $FeCl_3$-polymerization, **1** shows a strong induced optical activity in its π-π^* transition, provided the polymer is in its almost coplanar associated form. This association with a strong conformational rigidity, a prerequisite for a stable chirality from a helical structure of **1**, is found in poor-solvents as well as in the solid state. In a good solvent like $CHCl_3$ the disordered non-planar structure is optically inactive in its backbone. The transfer to an associated form is accompanied with solvatochromism and thermochromism in absorption, while significant changes in fluorescence behaviour and in the circular dichroism spectra are observed. All techniques show fine structure in the almost coplanar state while all absorptions are exciton coupled, reflecting the Davydov splitting of the coupled excited states.

INTRODUCTION

Following the first reports[1,2] on chiral conducting polymers in 1985, a number of these optically active structures has been studied in detail.[3-9] The introduction of chiral side chains at the 3-position of polythiophenes and polypyrroles has led to conjugated polymers featuring high optical rotations[4], up to $[\alpha]_D^{22} = 3000$. Furthermore, enantioselective doping processes are observed upon electrochemical oxidation of the optically active polymer using a racemic mixture of chiral anions.[4,10] All chiroptical studies reported so far are dealing with regiorandom polyheterocycles and an accurate understanding of the chiroptical properties is lacking.

3-Alkyl-substituted achiral polythiophenes have been studied in detail with respect to their solvatochromic[11] and thermochromic[12-14] behaviour. It is now well-accepted, that two distinct forms can be present depending on solvent and/or temperature; a predominantly coplanar structure (in an aggregated form) in a non-solvent or at low temperatures and a conformationally disordered non-planar structure in a good solvent or at higher temperatures.

Recently, new polymerization techniques have been developed to yield highly regioregular head-to-tail 3-alkyl substituted polythiophenes.[15-17] This regioregularity has led to polymers with enhanced crystallinity, that in turn gives rise to enhanced conductivities[18] up to 1000 S/cm after I_2 doping and polythiophenes with bandgaps as low as 1.7 eV have been reported.[19] The studies on regioregular polythiophenes in combination with our interest in chirality of optical materials[20] prompted us to investigate regioregular optically active polythiophenes. In this paper the synthesis, and chiroptical properties of 3-[2-((S)-2-methylbutoxy)ethyl]polythiophene 1 are described. This regioregular polymer is compared with the corresponding regiorandom optically active polymer 2. The latter has been reported previously; its optical properties, however, have not been discussed.[5]

SYNTHESIS OF OPTICALLY ACTIVE POLYTHIOPHENES

The syntheses of 1 and 2 are outlined in scheme 1. The starting material 3-thiopheneacetic acid is reduced with $LiAlH_4$ to yield 2-(3-thienyl)ethanol in 89%. The commercially available optically pure (S)-(-)-2-methyl-1-butanol is activated as a tosylate for the Williamson-ether synthesis yielding the optically active thiophene 3 in 83%. Compound 4 is obtained by selective iodination of 3 at the 2-position using I_2 in HNO_3 in a yield of 47% after destillation. Using McCullough's method,[15,16] by making the 5-lithio compound first, transforming it into the Grignard compound, followed by polymerization under the action of a catalytic amount of $Ni(dppp)Cl_2$ yields the raw polymer 1. Removal of low molecular weight and irregular fractions is obtained by successive extractions with methanol and hexane. A final extraction with $CHCl_3$ furnishes the pure regioregular 1 in 31% yield. The corresponding regiorandom isomer 2 is obtained by the $FeCl_3$-oxidative polymerization of 3 at −20°C. In this way two samples of 2 are prepared using different reaction times, 3 and 20 hours, respectively. In order to remove material that is slightly grafted, a number of washings and extractions has been carried out.

The molecular weight of 1, as determined by GPC against polystyrene standards, is estimated at $\overline{M}_n$ = 16,900 g/mol, D = 1.4. NMR spectroscopy allows the determination of the regioregularity of the polymers. The ^{13}C-spectrum of 1 shows that within the experimental error of the NMR experiment no evidence is found for the presence of irregular linkages in 1. The regiorandom 2 ($\overline{M}_n$ = 30,000 g/mol, D = 4.4 and $\overline{M}_n$ = 19,000 g/mol, D = 2,6) exhibits the well-known ratio of approx. 60% head-to-tail and 40% head-to-head and tail-to-tail linkages.
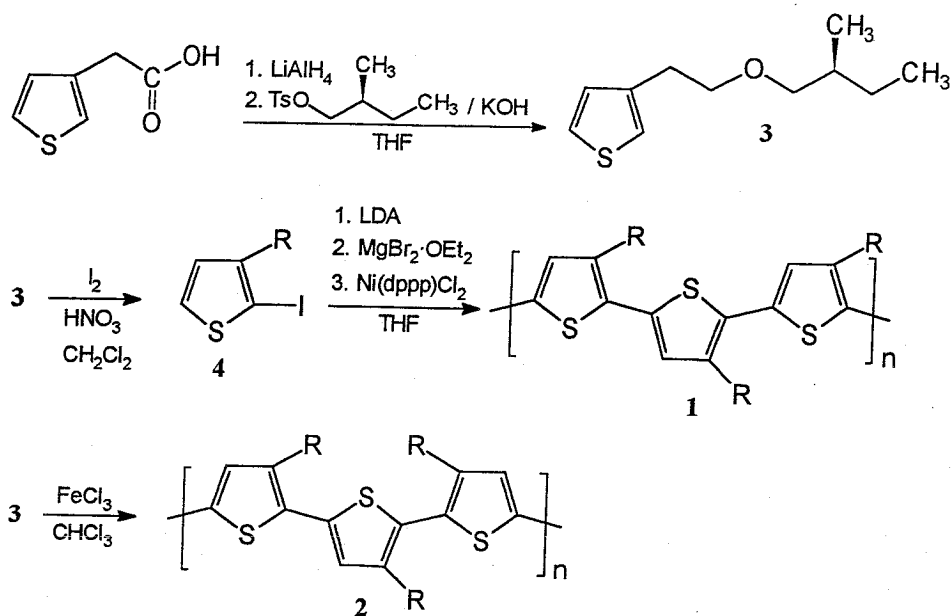
Scheme 1

ABSORPTION AND EMISSION SPECTROSCOPY

Absorption and emission spectra of **1** and **2** are recorded in good solvents ($CHCl_3$ or THF), in poor solvents (decanol-1 at room temperature and mixtures of $CHCl_3$-CH_3OH or THF-CH_3OH) as well as in the solid state. The electronic absorption spectrum, together with the fluorescence spectrum, of **1** in $CHCl_3$ is given in figure 1. In $CHCl_3$ the absorption maximum for **1** is found at 445 nm and the emission of **1** is centered around 600 nm, while some vibronic fine structure is observed. The excitation spectrum of **1** in $CHCl_3$ resembles the absorption spectrum to a great extent. For **2** the absorption maximum is found at 427 nm, reflecting a small decrease in effective conjugation length by a decrease in regioregularity. These data are all in full agreement with data of other regiorandom and regioregular polythiophenes published before[19-22]. In good solvents all polythiophenes are in a random-coillike and disordered, non-planar state.

Absorption spectra of cast films from $CHCl_3$ solutions of **2** exhibit only a minor shift of λ_{max} compared to solution; from 427 to 438 nm and some ill-defined low energy features are detected. Depending on the purity of the sample the intensity of the low-energy features differ. The spectrum of a film of **1** (figure 2a) exhibits three major absorption bands at 512, 540 and 592 nm, respectively, in stead of one peak at 445 nm in a $CHCl_3$ solution. In some cases similar bands are assigned to chains with different effective conjugation lengths,[13,23] others assign these three absorptions to vibronic bands of the π-π* transition.[11] This fine structure is more evident in the fluorescence spectrum of the cast film of **1** on sapphire at 80 K (figure 2b). The emission peaks are separated by 1300-1400 cm^{-1}, corresponding to the C=C vibration of thiophene.[11] The absorption and
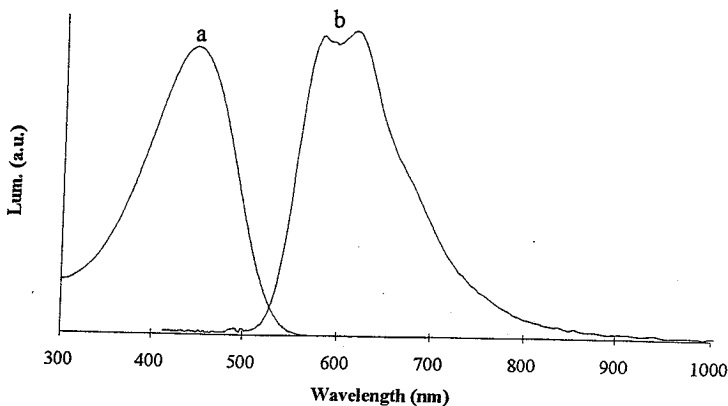
Figure 1. Absorption (a) and emission (b) spectra of **1** in CHCl$_3$. For (b) an excitation wavelength of 488 nm was used.

emission spectra of **1** in the solid phase at 80 K are all assigned to an associated almost coplanar state of the polymer, no features that can be attributed to parts of **1** that are disordered or non-planar are detected. It is evident that a regioregular polymer is more susceptible to form associated ordered structures than regiorandom polymers. The spectra of **2** in the solid state are interpreted as the result of polymer chains that are only for small portions in their associated coplanar state.
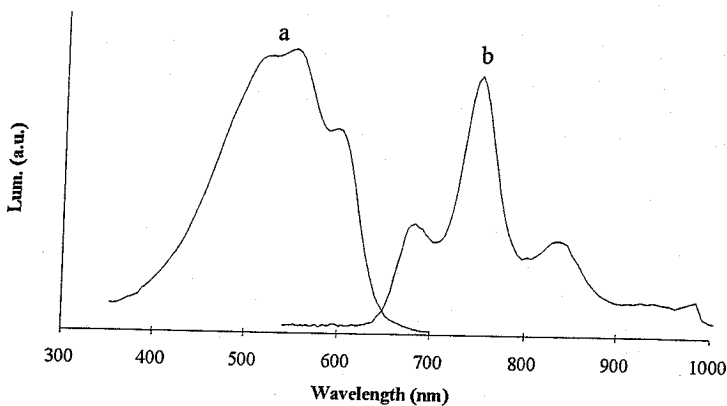
Figure 2. Absorption spectrum (a) of **1** on glass at room temperature and emission spectrum (b) of **1** on sapphire recorded at 80 K with excitation wavelength at 488 nm.

By using poor solvents or solvent mixtures, it is possible to obtain an associated form of **1** in solution and to modulate between associated ordered form and disordered from. These phenomena will be discussed in the context of solvatochromism and thermochromism.

SOLVATOCHROMISM AND THERMOCHROMISM

Upon the addition of CH_3OH to the $CHCl_3$ solutions of **1** a significant solvatochromism is observed and at a concentration of 61% CH_3OH the absorption spectrum in solution resembles that of **1** in the solid state to a great extent, although some remaining absorption assigned to a disordered fraction is detected (figure 3). An isobestic point is found at $\lambda = 473$ nm. A further increase of non-solvent gives rise to polymer precipitation. We found that the purity of the sample strongly influences the degree of well-ordered association in certain solvent combination. In some cases precipitation of **1** occurs already at a point that considerable amounts of disordered polymer with its absorption at 445 nm are still present. A variety of other poor solvents, like the n-alkanols, or solvent mixtures, like THF-CH_3OH, give rise to the formation of associated forms of **1** in solution as well.
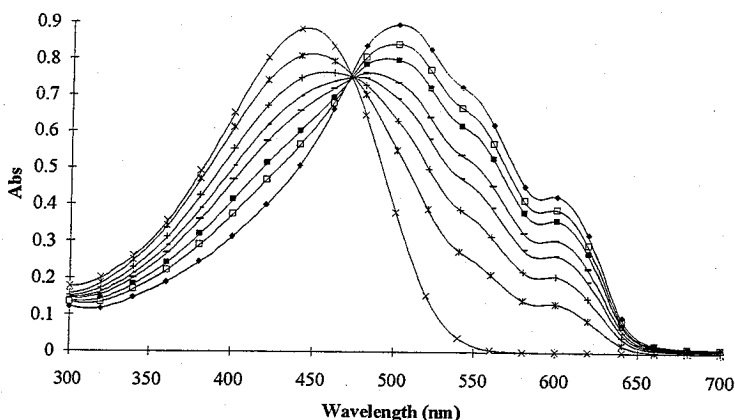

Figure 3. Absorption spectra of **1** in chloroform-methanol solutions. ($\times$) 100% $CHCl_3$, ($*$) 55% $CHCl_3$, ($+$) 54% $CHCl_3$, ($-$) 53%$CHCl_3$, ($\bar{}$) 52%$CHCl_3$, ($\blacksquare$) 50%$CHCl_3$, ($\square$) 47%$CHCl_3$, ($\blacklozenge$) 39%$CHCl_3$.

Thermochromism is observed for solutions of **1** in poor solvents as well as for **1** in the solid state. A typical experiment showing the thermochromism of **1** in decanol is presented in figure 4 and resembles the data published for other 3-substituted polythiophenes.[14] Only the high regioregularity in **1** makes the thermochromic changes more significant than in the case of polythiophenes that are less regioregular.

All the results presented above support the aggregation theory as presented by Wudl et al. for regiorandom 3-alkyl-polythiophenes,[11] however, it is more pronounced in the case of a highly regioregular structure. These trends towards more significant changes in the thermochromism by an increase in regioregularity has been put forward recently.[14] However, there is still much controversy on the topic of dynamics in these associated forms. By studying the chiroptical properties of optically active **1** we will make an attempt to disclose some of the unravelled features of 3-substituted polythiophenes in the solid phase.
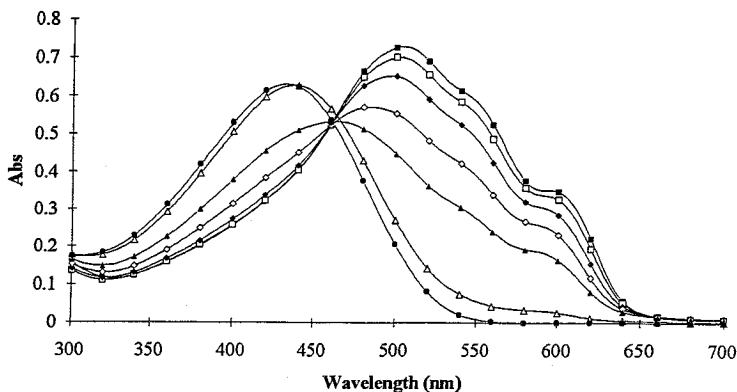
Figure 4. Absorption spectra of **1** in decanol. (■) 20°C, (□) 40°C, (◆) 60°C, (◇) 80°C, (▲) 90°C, (△) 100°C, (●) 120°C

CHIROPTICAL PROPERTIES

The remote distance of the stereocenter and the π-conjugated chain enables us to study the chiroptical properties of **1** in great detail. The π-π* transition at λ_{max} = 445 nm of **1** in CHCl$_3$ is optically inactive. However, upon the addition of CH$_3$OH to the CHCl$_3$ solution, the solvatochromism observed is accompanied by the appearance of strong Cotton effects in the Circular Dichroism (CD) spectra (figure 5). Hence, the associated coplanar state is observed in the CD spectra only, while in the UV/Vis spectra both the disordered and associated form are observed.
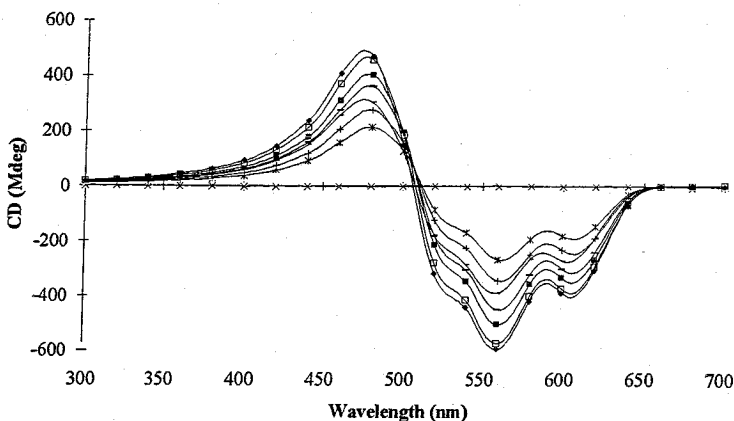

Figure 5. Circular Dichroism spectra of **1** in chloroform-methanol solutions. (×) 100% CHCl$_3$, (✳) 55% CHCl$_3$, (+) 54% CHCl$_3$, (-) 53%CHCl$_3$, (–) 52%, (■) 50%CHCl$_3$, (□) 47%CHCl$_3$, (◆) 39%CHCl$_3$.

These CD-spectra are interpreted as superpositions of three oscillator-coupled (exciton-coupled) CD bands with corresponding λ_{max} at 512, 540 and 592 nm, respectively. Apparently, all three bands are exciton-coupled and exhibit first a positive Cotton effect followed at higher wavelength by a negative Cotton effect. The exciton coupling results in a Davydov splitting of coupled oscillators for all bands of the excited state S_1.

Optical Rotatory Dispersion- and CD-spectra of a solution of **1** in 40% $CHCl_3$ - 60% CH_3OH are recorded to estimate chiroptical properties of **1** in detail. From the ORD-spectrum an $[\alpha]_{513}^{22}$ of 140,000 is estimated for $\lambda = 513$ nm. At the sodium D-line the estimated $[\alpha]_{589}^{22}$ is −9000, indicating the irrelevance of reports on optical rotation at one wavelength for these types of molecules. From the CD spectrum a chiral anisotropy factor at $\lambda = 625$ nm of $g = -2 \cdot 10^{-2}$ is estimated; an extremely high g-value for an electric dipole allowed transition.

ORD- and CD-spectra of **1** in the solid state are similar to those found in the solvent mixtures mentioned above. However, the chiral anisotropy factor is in most cases significantly lower for the solid state.
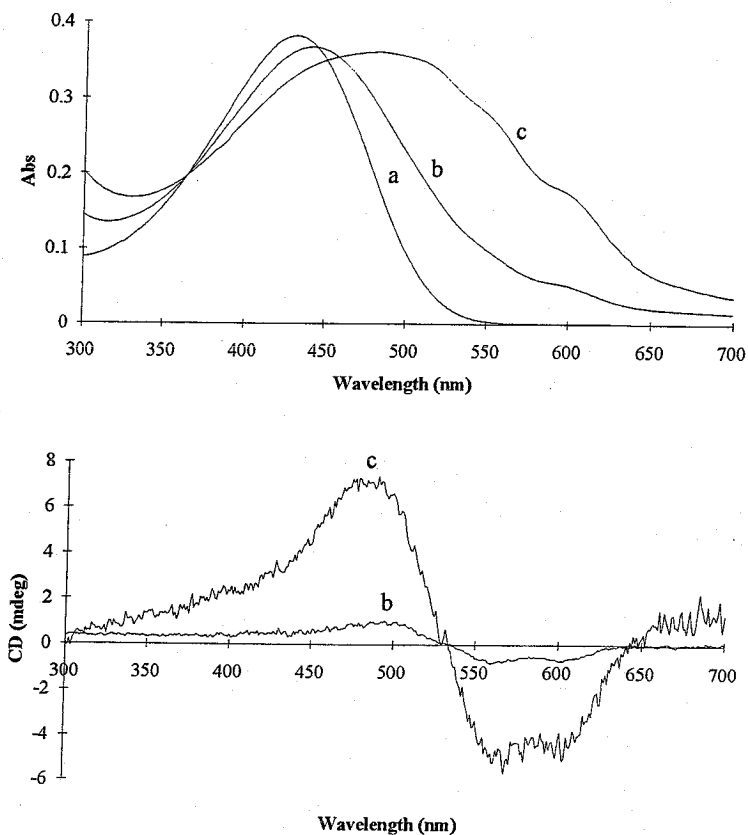

Figure 6. Absorption and Circulair Dichroism spectra of two samples of **2** in $CHCl_3$ (a) and in $CHCl_3$-CH_3OH (20% - 80%) (b) and (c).

ORD- and CD-spectra of the regiorandom samples of **2** in solution show similar phenomena. The magnitude of the effects, however, is much smaller. In the most ideal situation an $[\alpha]^{22}_{513}$ of 5000 and a g-value at $\lambda = 625$ nm of $-7 \cdot 10^{-4}$ are detected for **2**, only. The UV/Vis- and CD-spectra of two samples of **2** in CHCl$_3$ and CHCl$_3$-CH$_3$OH (20%-80%) are given in figure 6, showing that the optically active electronic transitions in **2** are situated at the same wavelength as in **1**. This implies that the major portion of **2** is still in its disordered state and only a small portion is in the coplanar optically active state.

The thermochromic transitions of **1** are investigated with CD-spectroscopy as well. A typical CD-experiment of a decanol solution of **1** is given in figure 7. The temperature range in which the disappearance of the CD effects occurs (90-110°C) is very similar to the temperature range in which λ_{max} shifts from 512 to 438 nm in the UV/Vis spectra. The optically active low-temperature phase, which has an UV/Vis spectrum resembling that of **1** in a solution of 40% CHCl$_3$ - 60% CH$_3$OH, is transformed into an optically inactive form at higher temperatures, showing the close resemblance between solvatochromism and thermochromism. Upon cooling the optically active coplanar form of **1** returns. The history of the sample determines the magnitude of the Cotton effects to a certain extent. Apparently, kinetic parameters in the association are of importance to the extent of induced chirality of the polythiophene backbone. Similar parameters determine the extent of induced chirality of **1** in the solid state.
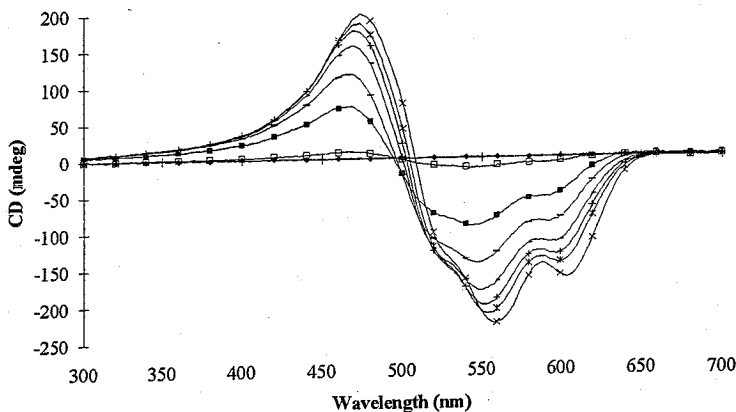

Figure 7. Temperature dependence of the Circular Dichroism of **1**. (×) 20°C, (✳) 50°C, (+) 60°C, (·) 70°C, (−) 80°C, (■) 90°C, (□) 100°C, (◆) 110°C.

DISCUSSION AND CONCLUSIONS

We have shown that significant induced optical activity in the π-π* transition of 3-substituted polythiophenes can be obtained, provided the substituents are positioned in a regioregular head-to-tail fashion. In the regiorandom structures the corresponding effect is significantly smaller. This strong induced optical activity is even more imposing, when the large distance between the stereocenter and the backbone and the small difference between the groups at the stereocenter are considered. Apparently, the polythiophene

backbone has become chiral and due to the presence of only one enantiomeric form in the side chain there is a strong preference for the backbone to form one chiral superstructure over the other. It is estimated that the difference in conformational energy for both diastereomeric forms is marginally small and the stable induced chirality can only be the result of a frozen-in conformation. It is proposed from the chiroptical data presented here, that only an aggregated form with a strong conformational rigidity in the polythiophene backbone can adopt this stable chiral conformation; a rigidity normally found in crystalline phases only. Hence, microcrystallites of 1 are thought to be formed.

The induced optical activity with its pronounced exciton coupling of all three bands is either the result of an intramolecular helical conformation of the backbone or the result of an intermolecular chiral orientation of predominantly coplanar polymer chains with a kind of supercoiling in the crystalline phase. Theory concerning exciton coupling[24,25] does not unambiguously distinguish between both modes. However, it is reasonable to assume that supramolecular architectures are responsible for these pronounced effects.

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