MODIFICATION OF THE PHYSICAL PROPERTIES OF POLYMERS BY SUPRAMOLECULAR INTERACTIONS

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Abstract: Using molecular recognition, receptors based upon diphenylglycoluril have been clipped onto paraquat polymers and styrene copolymers. In the case of the former polymers, the viscosity and electrochemical behaviour was modified. In the case of the latter, liquid crystallinity was induced upon complexation.

INTRODUCTION

Supramolecular chemistry is concerned with the design, synthesis and study of molecular systems and assemblies of molecules held together by relatively weak non-covalent interactions such as hydrogen-bonding, electrostatic and Van der Waals interactions (Refs. 1,2). In Nature there are many examples of large structurally complex systems that are built up using a variety of self-assembly processes based upon these relatively weak forces (Ref. 3). Although constructed in many different ways and performing a variety of different tasks the basic principles involved in their assembly are the same. In order to mimic the biomolecules and biomolecular complexes found in Nature and to understand their properties and functions, molecular recognition by synthetic receptor molecules, in solution and in the solid state, has received considerable attention (Ref. 4). In addition to serving as bio-models these receptor molecules can be expected to find applications as new types of catalysts, switches, sensors and storage devices. In the field of materials science, supramolecular interactions may be used to control physical properties such as liquid crystallinity or electrochemical behaviour by molecular recognition between molecules and macromolecules (Ref. 5). A number of recent studies describe the binding of protein molecules to specific domains of nucleic acid

chains (Ref. 6). Some of these proteins are dimers and possess the shape of a super clip or super tweezer, which can bind to single-stranded DNA chains and change the physical properties of these biomolecules (Ref. 7). These particular examples from Nature have inspired us to design molecular 'clips', which are capable of binding to functionalized polymer chains. It will be shown here that upon binding of these clips the physical properties of the macromolecules can be altered.

RESULTS AND DISCUSSION

Chart 1.

1

2

$$R = \quad \begin{array}{c} OC_{12}H_{25} \\ -OC_{12}H_{25} \\ OC_{12}H_{25} \end{array}$$

3

4

5

The clip molecules (1-3) used in this study were previously synthesized in our group (Ref. 8). They possess a concave framework containing two urea units and two methylene-linked aromatic walls.

Dihydroxybenzene molecules have been shown to complex within the cavities of these receptors by a combination of π-π interactions with the aromatic walls and hydrogen bonding to the urea carbonyl functions. In the case of clips of type **3**, which possess 1,8-naphthalene aromatic side-walls, the binding occurs via an induced fit mechanism. In solution this naphthalene clip exist as three conformers (*aa*, *as* and *ss*) which interconvert slowly on the NMR time scale (Ref. 9). Upon the addition of a guest molecule one of the walls of the receptor flips up to form a cleft which accommodates the guest (see Fig. 1).
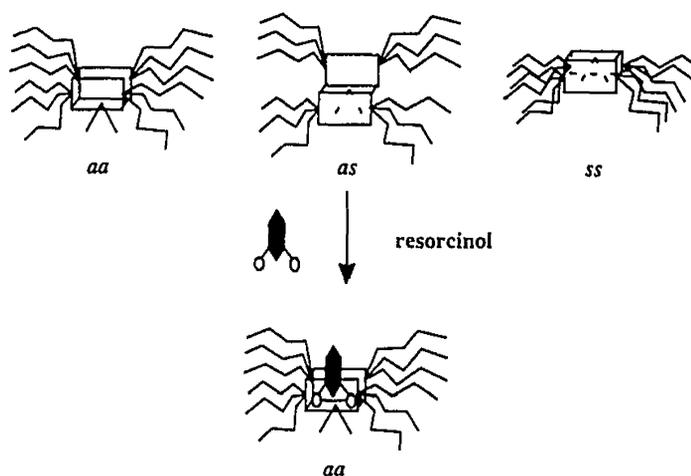
Fig. 1. Induced binding of resorcinol in molecular clip **3**

Compound **3** displayed a reversible crystalline to isotropic transition (K-I) at 159-164 °C. Only upon rapid cooling was a liquid-crystalline phase observed (Ref. 10). The complex of **3** with 1,3-dihydroxy-benzene (resorcinol), however, showed a smectic phase with a clearing temperature of 110 °C. This complex was found to be unstable upon repetitive heating and cooling. The addition of methyl 3,5-dihydroxybenzoate to **3**, gave a stable complex due to its increased binding strength and induced reversible liquid-crystalline behaviour. This behaviour could be modified by changing the host-guest ratio (Fig. 2.) At low concentrations of guest smectic mesophases were observed (birefringent mosaic type textures). At higher concentrations of guest only a nematic phase was visible (birefringent texture and a small enthalpy change in differential scanning calorimetry). Having found that the addition of two non-liquid-crystalline components can result in a liquid-crystalline complex, it was of interest to see if this liquid-crystalline behaviour could be induced in macromolecules.
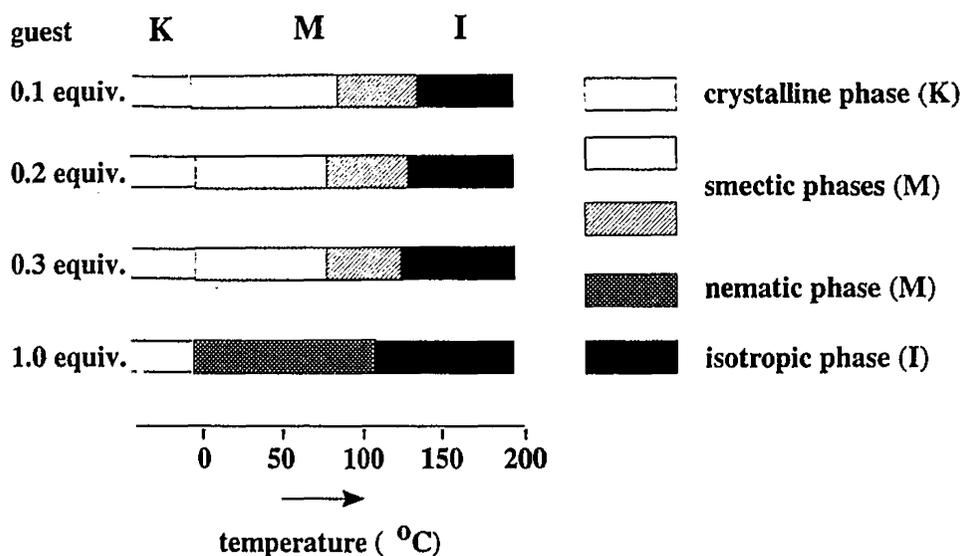
220

Fig. 2. Thermotropic liquid-crystalline behaviour of clip 3 in the presence of different amounts of methyl 3,5-dihydroxybenzoate

Two types of styrene and substituted styrene copolymers were synthesized (compounds 4 and 5, Chart 1). Copolymerization of styrene with 4-benzyloxystyrene in the presence of 2,2'-azo-diisobutyronitrile (AIBN) followed by deprotection and modification gave polymer 4 (weight-average molecular weight $\overline{M}_w$=24 000; ratio of weight- to number-average molecular weights $\overline{M}_w/\overline{M}_n$=2.38). In a similar way copolymerization of styrene with protected 3,5-dihydroxystyrene followed by deprotection afforded copolymer 5 ($\overline{M}_w$=35 500; $\overline{M}_w/\overline{M}_n$=2.26). Both these copolymers did not exhibit any liquid-crystalline behaviour.

Upon complexation of molecular clip 3 to copolymer 4 (mole ratio 1:1) a very stable liquid-crystalline phase was induced. This phase was observed from 30 to 140 °C and possessed a typical discotic texture, clearly different from the smectic phase seen for the complex with the methyl dihydroxybenzoate (Fig. 3A). In the case of the second copolymer 5, the dihydroxybenzene moities are directly attached to the polymer backbone. Clipping of one molecule of receptor 3 to every second 3,5-dihydroxybenzene unit of 5 also induced a discotic phase from 86 to 131 °C. In contrast to 4 an additional more highly ordered discotic phase from 21 to 86 °C was observed (Fig. 3B). These results clearly indicate that liquid crystallinity can be induced in a polymer by a process of molecular recognition.
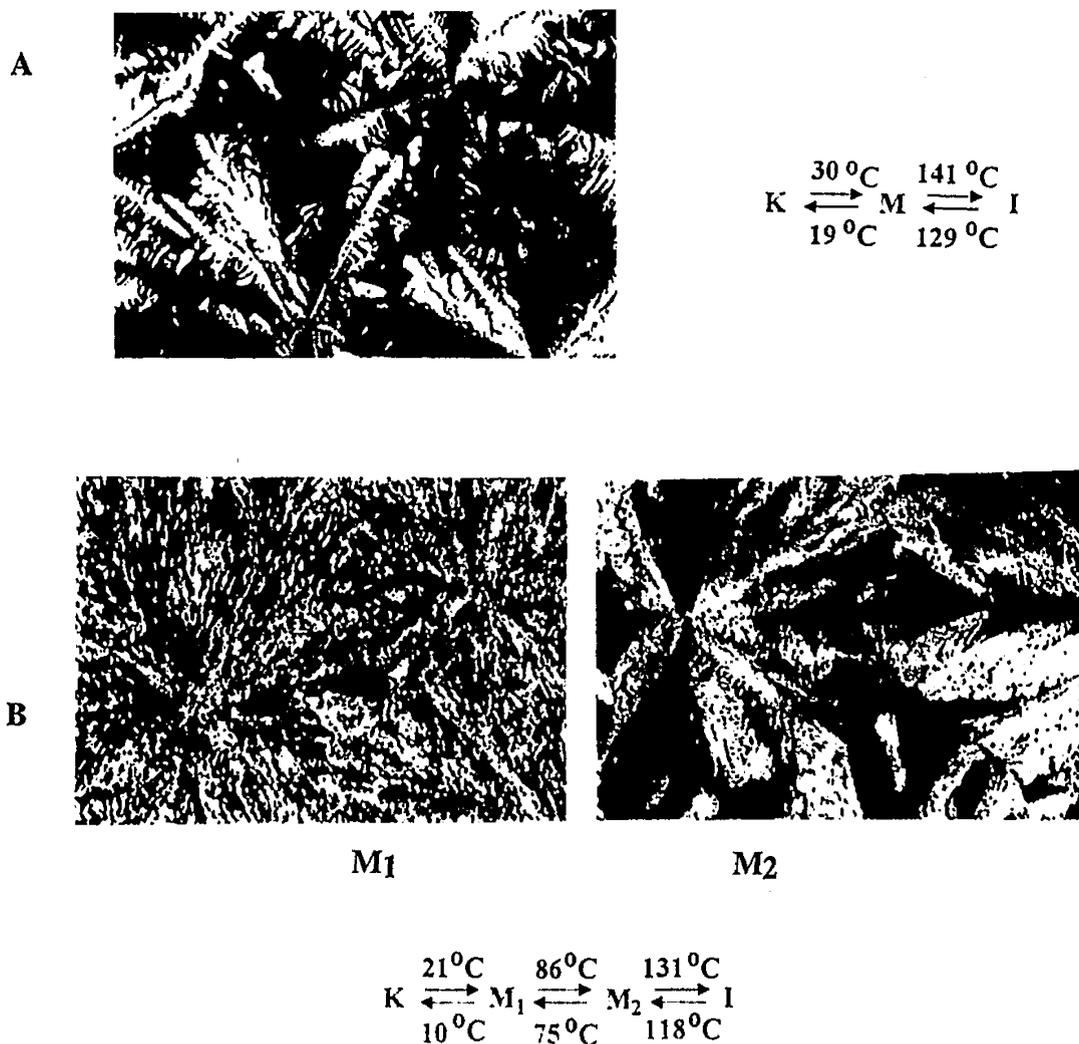
A

$$K \underset{19\,^{\circ}C}{\overset{30\,^{\circ}C}{\rightleftharpoons}} M \underset{129\,^{\circ}C}{\overset{141\,^{\circ}C}{\rightleftharpoons}} I$$

B

M1   M2

$$K \underset{10\,^{\circ}C}{\overset{21\,^{\circ}C}{\rightleftharpoons}} M_1 \underset{75\,^{\circ}C}{\overset{86\,^{\circ}C}{\rightleftharpoons}} M_2 \underset{118\,^{\circ}C}{\overset{131\,^{\circ}C}{\rightleftharpoons}} I$$
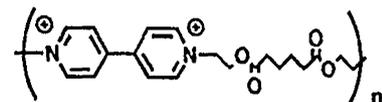
Fig. 3. Induced polymeric liquid-crystalline behaviour with clip 3 for (A) polymer 4 and (B) polymer 5

Polymeric paraquats are well known examples of ionene polymers and have been investigated as redox active films and more recently as optical data storage materials. They exhibit a wide range of electrochromic and thermochromic behaviour (Refs. 11-13). We have recently found that molecular clips of type 2 can be complexed to these charged paraquat polymers. Receptor 2 possesses a crown ether moiety and has the shape of a basket. These baskets have been previously found to bind alkali metal ions and protonated amines in addition to aromatic guests (Ref. 14). Molecular binding of paraquat (6), is currently of great interest. This compound has been

incorporated in a series of elegant catenands and rotaxanes by the group of Stoddart (Ref. 15). Molecular basket **2** was found to be an exceptionally good host for the complexation of paraquat, with a binding constant greater than 50 000 M^{-1}. X-ray crystallography and ^1H NMR confirmed that the paraquat is bound within the basket-shaped cavity of **2**. The electrochemical behaviour of **6**.(PF6)2 was modified by complexation with **2**. The guest **6** showed two reversible one-electron transfers $E_{1/2}$ $(2^+/1^+)$ = -0.423 V, $E_{1/2}$ $(1^+/0)$ = -0.840 V. Upon the addition of 1 equivalent of basket **2** the first redox potential was shifted by more than 100 mV to more negative potential whereas the second potential remained unaltered. The receptor stabilizes the doubly charged paraquat species, but once reduced, the guest dissociates and consequently the second potential is unaltered.

Polymers **7** and **8** were synthesized by the reaction of dibromoalkanes with bipyridine using literature procedures (Ref. 11). Polymer **9** was prepared by the condensation of N,N'-bis(2-hydroxyethyl)-4,4'-bipyridinium hexafluorophosphate with 1 equivalent of adipoyl chloride in acetonitrile. Ultraviolet binding studies in acetonitrile showed that **2** can be clipped to polymeric paraquats **7**, **8** and **9** with association constants of 1 800 M^{-1}, 4 500 M^{-1} and 19 000 M^{-1} (per polymer repeat unit), respectively (Tab. 1).

Tab. 1. Binding constants of complexes of **2** with paraquat and polymeric paraquats [a]
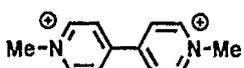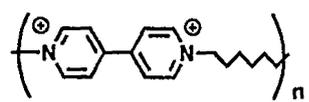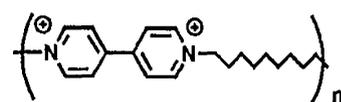
		K_a/M^{-1}
6		57 000
7		1 800
8		4 500
9		19 000

a) In acetonitrile; n=5-12; K_a is per polymer repeat unit

Viscosity measurements revealed that the specific viscosity of the polymers **7** and **8**, solubilized in acetonitrile, increases upon the addition of 0.03 equivalents of receptor **2** per repeat unit, suggesting that the molecular weight of the polymer increases upon complexation with **2**. The redox potentials of the polymers were also influenced by the complexation of the receptor. Polymer **7** displayed in acetonitrile two redox transitions: $E_{1/2}$ $(2^+/1^+)$ = -0.387 V, $E_{1/2}$ $(1^+/0)$ = -0.840 V. Upon the addition of 1 equivalent of **2** per repeat unit the first redox potential was shifted 20 mV to more negative potential, the second potential remaining unaltered. Addition of 3 equivalents of **2** resulted in a 35 mV shift in the negative direction. These shift values are smaller than the 100 mV shift measured for the paraquat monomer which may be a result of the lower binding affinity of **2** for the polymeric paraquat.

CONCLUSION

We have shown that molecular recognition can be used as a tool for the modification of the physical properties of polymers. Using relatively simple molecular receptors based upon diphenylglycoluril, liquid crystallinity can be induced in copolymers of dihydroxy-styrene and styrene. As far as we are aware this is one of the first examples of liquid-crystalline behaviour induced in polymers by molecular recognition. Using molecular receptors possessing crown ether moieties the electrochemical behaviour and viscosity of ionene polymers can be manipulated. The combination of supramolecular chemistry and polymer chemistry opens a new and exciting area offering the opportunity to manipulate and hence tune the physical properties of macromolecules and to create new and exciting materials.

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