

# ADDITION COMPOUNDS AND COMPLEXES WITH POLYMERS AND MODELS

ROLF C. SCHULZ

*Institute of Macromolecular Chemistry,  
Technische Hochschule Darmstadt, D 61 Darmstadt, FRG*

with contributions by

D. FLEISCHER, A. HENGLEIN, H. M. BÖSSLER, J. TRISNADI and H. TANAKA

## ABSTRACT

Most chemical transformations of polymers consist of either the formation or the splitting of covalent bonds. There are other reactions with polymers, however, which depend upon the reversible formation of adducts or complexes. Several examples of these types of addition compounds or complexes with polymers are described. Lanthanide complexes with homopolymers and with copolymers of ring acetal (trioxane, dioxolane, trioxocane, etc.) bring about signal shifts and splitting in  $^1\text{H}$ - and  $^{13}\text{C}$ -n.m.r. spectra. These make it possible to obtain important information about microstructure and sequences.

Iodine produces coloured addition compounds with various polymers. Newer results are presented concerning the kinetics of the iodine-amylose reaction, which were examined with the assistance of pulse radiolysis.

Iodine-amylose shows strong induced Cotton effects in o.r.d. and c.d. These depend upon the helical structure of the inclusion compound.

Polysaccharides form complexes with Schweizer reagent or with other heavy metals as well. The structure of the Cu-amylose complexes is deduced from the changes in the optical rotation and from the induced Cotton effects.

Even adducts between amylose and several azo dyes show strong induced Cotton effects. The composition of these adducts, the equilibrium constants and dissymmetry factors have been determined.

Finally various types of EDA complexes from polymer donors and/or acceptors are depicted. Our own research is concerned with polymer and oligomer esters with spirocyclic fluorene or tetranitrofluorene groups.

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## INTRODUCTION

There is a large number of chemical reactions with polymers. They are mainly carried out for the purpose of modifying physical and technical properties. But these reactions can also serve in explaining the composition and structure of homopolymers or the sequence of copolymers. In much of the research done in this area functional groups are introduced in order that these reactive polymers may be utilized as exchange resins, as supports for enzymes or solid phase syntheses, or for the preparation of graft copolymers.

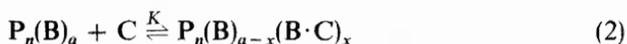
By far the greater number of these reactions on macromolecules include

either solvolyses, eliminations or rearrangements as well as nucleophilic or electrophilic substitutions. They consist accordingly in the formation and/or splitting of covalent bonds. Most of these reactions are irreversible. They can be described through the following equation :



In this equation  $P_n(X)_a$  signifies a polymer molecule with a functional group X which is transformed to group Y by means of the reagent R. The conversion is frequently incomplete and a small amount of the original group remains unchanged in the reaction product.

In addition to these reactions there are several transformations with polymers which involve the formation of complexes or adducts. No covalent bonds are formed in these, but instead they contain heteropolar bonds, chelates, H-bonds, c.t.-complexes, etc. These reactions are generally reversible and lead to equilibria. They can be described through the following schematic equation :



This means that a complex-forming, low molecular weight compound C together with a certain number of functional groups B in polymer  $P_n$  form a complex  $(B \cdot C)$  in a reversible reaction. Here too, it is possible that a fixed number of groups B remains uncomplexed.

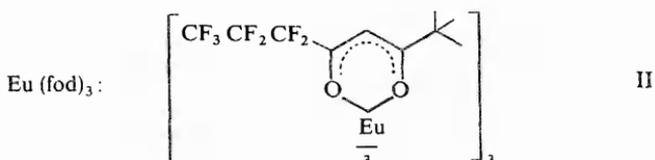
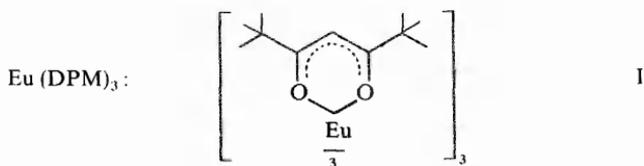
In low molecular weight complexes the equilibrium constant is dependent upon the chemical nature of the components B and C, and upon the solvent and temperature. In related polymer complexes it has been demonstrated that the structure of the polymer, the tacticity and the secondary structure as well as the degree of polymerization also have a great influence upon the equilibrium constant. Sometimes the complex formation takes place only with polymers above a fixed degree of polymerization while oligomers or low molecular weight model compounds are not capable of complex formation.

Frequently the properties of the polymers are considerably altered through complex formation, even when the equilibrium constant is very small. The number of complexed groups is determined spectroscopically. On the other hand complex formation can also be used for analytic purposes. Several of these polymer complexes have a technical significance, e.g. in electrophotographic techniques. Of course reversible complex and adduct formation with macromolecules also plays an important role in many biochemical processes and enzyme reactions. It is also the basis of the very recent and important affinity chromatography. Several reactions of the type of equation 2 will be described in the following report. The examples are taken from the literature or from our own research, and they apply to synthetic as well as to naturally occurring polymers.

## LANTHANIDE COMPLEXES WITH POLYACETALS

It had been known for some time that paramagnetic transition metal ions had a very strong influence on signals of complex-bonded ligands in the  $^1\text{H}$  n.m.r. spectrum. But it was only through the systematic research done by

Hinkley<sup>1</sup> that the practical importance of these shifts was generally known. Since then, the so-called 'shift reagents' have become important in n.m.r. spectroscopy<sup>2</sup>. Various complexes of europium or praseodymium are the most frequently used (formulae I and II).

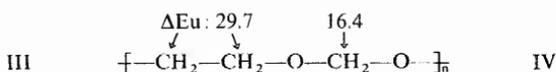
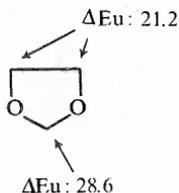


In these chelates, two coordination positions are still unoccupied. Therefore, they may add two molecules bearing nonbonded electron pairs (for example, amines, alcohols or ethers). Within these coordination complexes, the protons of the ligands are not only exposed to the external field but also to the magnetic field of the paramagnetic central ions (eg.  $\text{Eu}^{3+}$ ,  $\text{Pr}^{3+}$ ). The intensity of this additional field depends on the distance and the angle between the ligand proton and the central ion as well as on the concentration of the complex. Consequently, normally identical protons may show different shifts in the n.m.r.-spectrum according to their geometrical position within the coordination complex, which results in a very differentiated splitting of the signals and thus in a gain of information.

As already mentioned, the isotope shift  $\delta_{\text{exp}}$  also depends among other things on the concentration of the lanthanide chelate [L]. By measuring  $\delta_{\text{exp}}$  with varying chelate concentrations, the equilibrium constant  $K$  for the complex formation as well as the shift for a lanthanide (L) to substrate (S) ratio of 1:1 may be determined under specific conditions<sup>2, 3</sup>. This ratio is called the  $\Delta\text{Eu}$ -value. This value is very useful for the assignment of the signals, being characteristic of each proton within a specific complex. Although shift reagents have nearly always been used for low-molecular compounds up to now, they have also been found to be very valuable for elucidating polymer structures<sup>4</sup>.

In the following, it will be demonstrated by some examples that by means of complex formation between europium chelates and polyacetals it is possible to identify sequences up to 7 base units using n.m.r. spectroscopy, and to determine them quantitatively.

In the n.m.r. spectra of 1,3-dioxolane (III) and polydioxolane (IV), two singlets appear respectively which are to be assigned to the protons of the formaldehyde or the ethylene oxide units. When adding  $\text{Eu}(\text{DPM})_3$ , both signals are shifted by certain amounts. The shift intensities of the ethylene and methylene protons, expressed by  $\Delta\text{Eu}$ -value<sup>5</sup>, are as shown in the



formulae III and IV. In the  $^1\text{H}$  n.m.r. spectrum of a trioxane-dioxolane copolymer (Figure 1) four peaks appear<sup>5</sup>. The three singlets between  $\delta = 4.74$  and  $\delta = 4.89$  p.p.m. originate in the protons of the formaldehyde unit, three different arrangements of which can be found in these copolymers. More explicitly, it is neighbored either by two other methylene units, or by one methylene unit and one ethylene unit, or by two ethylene units. The signal (E) with  $\delta = 3.73$  p.p.m. is to be assigned to the ethylene protons of the dioxolane unit. When  $\text{Eu}(\text{DPM})_3$  is added to the polymer solution, this singlet is split up into three lines (Figure 2).

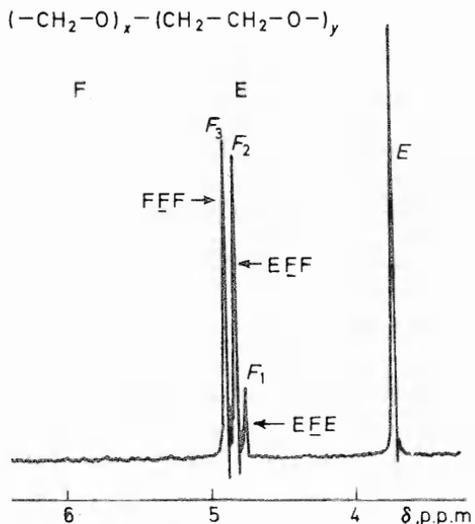


Figure 1. 60 MHz  $^1\text{H}$  n.m.r. spectrum of a trioxane-dioxolane copolymer in  $\text{CDCl}_3$  (62.5 mol % trioxane)  $F_1$ :  $\text{EFE}$ ;  $F_2$ :  $\text{EEF}$  and or  $\text{FEE}$ ;  $F_3$ :  $\text{FFF}$ .

Again, this splitting can only originate in the varying neighbourhood of the ethylene units. As each ethylene unit, however, can only be placed between two  $\text{CH}_2\text{O}$  units and, consequently, only one triad with  $\text{EFE}$  is possible, this splitting must be caused by more distant units. Therefore, heptads must be taken into consideration. By means of the  $\Delta\text{Eu}$ -values and the copolymerization statistics, the signals could be assigned to the following heptads:



Recently, Fleischer<sup>6</sup> was able to demonstrate that shift reagents also led to

## COMPLEXES WITH POLYMERS AND MODELS

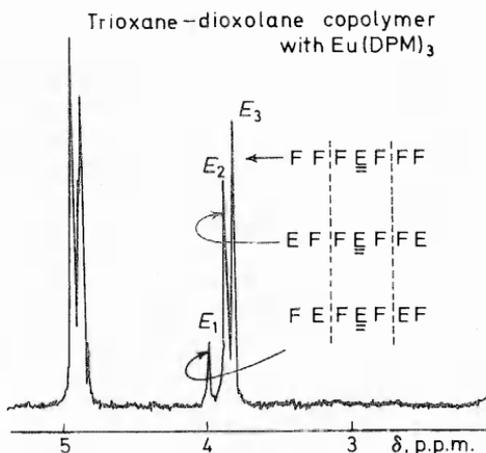
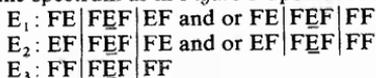


Figure 2. The same spectrum as in Figure 1 upon addition of  $\text{Eu}(\text{DPM})_3$



further splittings of the resonance signals in the  $^{13}\text{C}$  c.m.r. spectra of polyacetals. The  $^{13}\text{C}$  spectrum of the above-mentioned trioxane-dioxolane copolymer shows instead of four signals as in the proton spectrum, eight signals which can be assigned to pentads of methylene- and ethylene-oxide units. On addition of  $\text{Eu}(\text{fod})_3$ , the eight signals are split up into 10–13 signals. These can again be assigned to sequences of seven basic units. The assignments following from the proton spectra are not only confirmed but also supplemented, the splitting being so extensive in the methylene signal region as to make heptads perceptible. Moreover, the proportions of these sequences may be determined quantitatively, thus permitting an extensive elucidation of these polymer and copolymer structures<sup>6</sup>.

By means of shift reagents, the overall structure, the quantity of monomer diads (DOL-DOL; DOL-TOC and TOC-TOC) as well as the sequences of methylene and ethylene units of trioxane(TOC)-dioxolane (DOL) copolymers were determined in a similar way<sup>7</sup>.

## IODINE COMPLEXES WITH SOME POLYMERS

There are some synthetic and naturally occurring polymers which produce intense colour reactions with iodine either in aqueous solution or in the solid state. These reactions are reversible, and the iodine can be easily removed. These reactions therefore are of the type depicted in equation 2, in which the kind of complex or adduct formation depends upon the respective polymers. Iodine adducts are formed for example with polyamides<sup>8</sup>, polyethyleneoxide<sup>9</sup>, polyvinylalcohol<sup>10</sup>, polyvinyl carbazole<sup>11</sup> and some polysaccharides.

In 1927, the blue polyvinylalcohol-iodine complex was discovered simultaneously by Staudinger *et al.*<sup>12</sup> and by Herrmann and Haehnel<sup>13</sup>. This complex is of practical importance as an antiseptic in medicine and in the

production of polarizing sheets<sup>14</sup>. It is also used for analytical purposes in the determination of polyvinylalcohol<sup>15</sup>. Following a proposal made by Zwick<sup>10</sup>, the polyvinylalcohol-iodine complex is presumably composed of helical segments of the polymer, in the hollow cavities of which are included extended chains of associated iodine molecules. This structure is stabilized through the addition of boric acid. The rate of complex formation, the structure of the complex, the wavelength of the absorption maxima and its extinction coefficient are dependent upon various parameters. The influence of the tacticity, molecular weight and branching of polyvinyl alcohol, and of the content of residual acetyl groups upon the complex formation with iodine, has been studied in numerous recent papers<sup>16</sup>. The solutions are deep blue, green, red-orange or yellow, depending upon the conditions. The absorption maxima appear at 600–620 nm, 650–680 nm, 480–500 nm and approximately 350 nm. Recently, experiments on the resonance Raman spectra of the polyvinylalcohol-iodine complex have also been published<sup>17, 18</sup>. However, this method mostly furnishes information about the structure of the enclosed iodine atom but does not say very much about the structure of the polymers.

The deep blue colour which appears when mixing a dilute aqueous solution of starch and iodine has been known for over a hundred years<sup>19</sup>. In spite of many experiments, the cause of this colour reaction remained uncertain for a long period of time. In 1939 Freudenberg<sup>20</sup> suggested that a helical inclusion compound could be the structure for the colour complex. In 1944 this hypothesis was verified by Rundle *et al.*<sup>21</sup> with the help of x-ray diffraction. The accepted model for the solid state is a complex composed of a helix with six glucose units per turn. A chain of 10–15 iodine atoms is packed in the tube-shaped interior. On the average, 6–8 glucose units are associated with two iodine atoms.

It follows from various experiments that the amylose-iodine complex in a dilute aqueous solution has a very similar structure, and consists of helical segments with included iodine chains. It is to be emphasized that the iodine complex is formed only above a certain degree of polymerization ( $DP > 12$ ) (i.e. oligomers produce no colour reaction with iodine). Furthermore the absorption maximum of the complex increases with the DP. With the  $DP > 100$ , a maximum at approximately  $\lambda = 640$  nm is eventually attained<sup>22</sup>. The colour reaction is thermoreversible. Above 70 °C the colour of the solution fades and on cooling the blue colour appears again. For further details, the original papers or reviews should be referred to<sup>19, 23–25</sup>. In the following only two problems will be dealt with, viz. the kinetics of complex formation and the optical activity of the complexes.

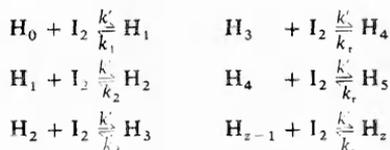
It was of course known previously that the reaction between iodine and amylose proceeds very rapidly, but it was not until 1970 that quantitative kinetic measurements were published for the first time by Hiromi *et al.*<sup>26</sup> as well as by Thompson and Hamori<sup>27</sup>. They made use of the stopped-flow method. The dead time of the instruments was only 0.5 ms and with an amylose concentration of 0.025 per cent and an iodine concentration of  $10^{-5}$  molar, the complex formation was already as much as 50 per cent completed within the dead time. For that reason Hamori *et al.* used much smaller amylose and iodine concentrations in order to slow down the reactions.

Henglein *et al.*<sup>28</sup> used pulsed radiolysis for these measurements. With this method the time resolution is from 10 to 100 times better, i.e. from  $10^{-4}$ – $10^{-5}$  s. Aqueous solutions of amylose containing  $10^{-2}$  mol KI were irradiated with a short pulse of 1–30  $\mu$ s of high energy electrons. Within this time a definite amount of molecular iodine is formed from the initially produced OH-radicals and the iodine ions. The iodine reacts with the amylose forming the coloured complex. The increase of extinction with time at certain wavelengths is indicated on an oscillograph with a time scale of from 0–0.5 ms. The results are discussed with reference to the mechanism suggested by Thompson and Hamori<sup>27</sup>.

As a result<sup>28</sup> an equilibrium should very quickly be attained between free iodine and the empty helices ( $H_0$ ) whereby, in a first stage, unstable complexes with 1–3 molecules of iodine per helix are produced ( $H_1$ ,  $H_2$ ,  $H_3$ ) (see scheme 1). Additional iodine is taken up into these  $H_3$  complexes, until iodine chains of approximately 7 iodine molecules ( $H_7$ ) are formed. When more than 4 iodine molecules are included, the reverse reaction is so small as to be unobservable.

The diffusion of the iodine molecules into the empty helices follows with a rate constant  $k'$  of approximately  $10^9$  l mol<sup>-1</sup> s<sup>-1</sup> which corresponds to a diffusion controlled reaction (Scheme 1). At low iodine concentrations

Thompson–Hamori mechanism for iodine–amylose reaction



( $H_n$ : helical segment with  $n$  iodine molecules)

Kinetics of  $I_2$  uptake into amylose helices ( $H_z$ ) (A. Henglein *et al.*)

$$\text{at } [I_2]: \sim 10^{-6} \text{ mol l}^{-1} \quad \frac{d[H_z]}{dt} \sim k' [I_2]^4$$

$$\text{at } [I_2]: \sim 10^{-4} \text{ mol l}^{-1} \quad \frac{d[H_z]}{dt} \sim k' [I_2]$$

$$k' \sim 10^9 \text{ l mol}^{-1} \text{ s}^{-1} \\ \text{amylose: } 0.025\% ; [C_6H_{10}O_5]: \sim 10^{-5} \text{ mol l}^{-1}$$

Scheme 1. Mechanism and kinetics of amylose–iodine reaction

( $\sim 10^{-6}$  mol l<sup>-1</sup>) the initial rate of the reaction is proportional to between the fourth and fifth power of  $[I_2]$ . At high iodine concentrations ( $\sim 10^{-4}$  mol l<sup>-1</sup>) the reaction is of first order with respect to  $[I_2]$ .

Our further experiments deal with the optical activity of the amylose–iodine complexes. Like all other polysaccharides amylose is optically active, since

each base unit contains five asymmetric carbon atoms. As the wavelengths decrease, the rotation values steadily increase<sup>29</sup>. This results in a so-called 'plain' rotatory dispersion curve, since amylose contains no chromophoric groups which absorb between 800 and 200 nm. A chiral secondary structure, such as a helix, contributes essentially to the rotation value as well, but in this case it cannot be separated from the basic rotation. In the circular dichrogram no Cotton effects appear and therefore no conclusions can be drawn from the o.r.d. and c.d. measurements about the secondary structure of the amylose. If, nevertheless, the helix model holds true for the amylose-iodine complex, then the chiral helix should asymmetrically induce the electron transitions of the enclosed chain of iodine atoms. Therefore the normally optically inactive iodine chromophore must become optically active in the inclusion compound and must exhibit a so-called 'induced Cotton effect'. This prediction, as a matter of fact, proves to be correct<sup>30, 22</sup>. The rotation values at 600 nm are approximately three times greater for the amylose-iodine complex than for pure amylose. And in this region too a maximum in circular dichroism appears which is lacking in pure amylose.

We have studied in detail the chiroptical properties of iodine-amylose and moreover have examined the dependence of the induced Cotton effects upon the iodine concentration, upon the molecular weight of the amylose, upon the solution and upon other parameters. The following are the most important results: (i) the optical activity is greatest in a proportion of 1 I<sub>2</sub> to 7 or 8 glucose base units; (ii) the wavelength for the long-wave Cotton-effect increases with the polymerization degree of the amylose; (iii) the circular dichroism ( $\Delta\epsilon$ ) is dependent upon the degree of polymerization and has a sharp maximum at a DP of 70-90; (iv) the induced Cotton effects appear only when an amylose-iodine complex is formed.

These results can only be explained by accepting the hypothesis of helical iodine inclusion compounds. They further confirm a model of the so-called interrupted helix much discussed at the present time; it is composed of many long inflexible helical sections with short intervals of randomly coiled segments between them<sup>19</sup>.

## METAL COMPLEXES WITH POLYSACCHARIDES

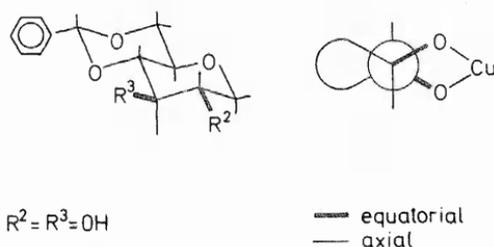
It is well known that many biopolymers, particularly enzymes, form very stable heavy metal complexes and they are biologically effective only in the presence of these metals. Many synthetic polymers likewise form various kinds of metal complexes. In the following, several complexes with polysaccharides will be very briefly covered.

In 1857, Schweizer<sup>31</sup> observed that cellulose dissolves in an ammoniacal copper tetramine solution. A copper-cellulose complex is thereby formed, which contains one copper atom for each glucose base unit. The complex is destroyed by acidification and the cellulose is precipitated. At a later date still other cellulose solvents were discovered, consisting of aqueous solutions of basic cadmium or iron complexes<sup>32</sup>. These soluble cellulose heavy metal complexes play an important role in cellulose chemistry, for example, in the production of synthetic fibres and in determining molecular weight<sup>32</sup>.

It is very surprising that amylose does not dissolve in the Schweizer

reagent. Instead an insoluble complex is formed, about whose structure nothing was known up to now. It can be demonstrated that the amylose-copper complex does not precipitate when mixing a very dilute solution of Schweizer reagent and amylose (amylose concentration about  $10^{-3}$  mol glucose units  $l^{-1}$ ). In examining the composition and structure of the complex, we again made use of the rotatory dispersion and the circular dichroism. Here too appear considerable deviations from the normal o.r.d. curve of amylose as well as several induced Cotton effects<sup>33</sup>.

It must therefore be a chiral complex. If the difference of the optical rotation between amylose and the amylose complex is plotted as a function of the molar fraction of copper (according to JOB) then maximum deviations are found at a mole ratio for glucose:Cu of 1:1. The overall composition is therefore the same as for the copper complex of cellulose. An inclusion compound, such as that formed with iodine, is very unlikely with this mole ratio. The measurements of circular dichroism have a big advantage in that the Cotton effects can also give some evidence about the configuration of the complex. According to investigations made by Bukhari *et al.*<sup>34</sup> on copper complexes of sugar derivatives, a short-wave negative c.d. peak and a long-wave positive peak occur when the complex is formed with hydroxyl groups in a bis-equatorial position (Scheme 2). As a matter of fact with the



Scheme 2. Chiral copper chelate with bis-equatorial OH groups in sugar derivatives

copper-amylose complex we find a weak positive Cotton effect above 600 nm and a strong negative Cotton effect at 280 nm. In the C<sub>1</sub>-conformation of the glucose units in amylose only OH groups on the C<sub>2</sub> and C<sub>3</sub> atoms are in the required bis-equatorial position. With this it clearly follows from the circular dichroism measurements that a chiral copper complex is formed from the Schweizer reagent and amylose with both secondary OH groups of the same base unit.

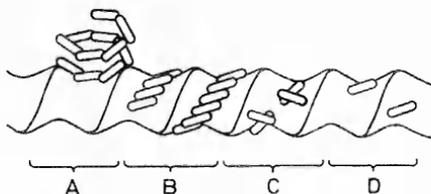
We have further examined complexes of amylose with cobalt amines<sup>33</sup>. These too show abnormal optical rotatory dispersion and several overlapping Cotton effects. In this case, however, it was not possible to determine the composition, since presumably several different complexes are formed and the equilibria between the various chelates are reached only very slowly.

However, in these cases the chiroptical properties can be traced back to the individual asymmetrical base units and no polymer effect or influence of secondary structure can be observed.

## AMYLOSE COMPLEXES WITH AZO COMPOUNDS

Some dyes show great affinity to cellulose which bonds them very firmly. They are called direct dyes. Although this dye bonding is very important for cotton dyeing, we have as yet no exact knowledge about the bonding forces<sup>35, 36</sup>. On the other hand, we know that certain dyes form salt-type compounds with polypeptides<sup>37</sup> or nucleic acids<sup>38</sup>. The chiroptical properties of these polymer-dye adducts furnish information about the secondary structure and helix-coil transformations of the polymers. Consequently, we tried to apply these methods also to polysaccharide-dye adducts<sup>39</sup>. Of course, only soluble polymers are suitable, so we chose amylose first. The aim was to get information about the amylose structure and the composition of the dye adducts. Because of the size of the dye molecules it was to be expected that the adducts could not be inclusion compounds of the iodine-amylose type.

For the interaction between a helical macromolecule and dye molecules four models are to be considered, shown in *Scheme 3*. Model A signifies that



*Scheme 3*. Different models for dye-polymer interaction

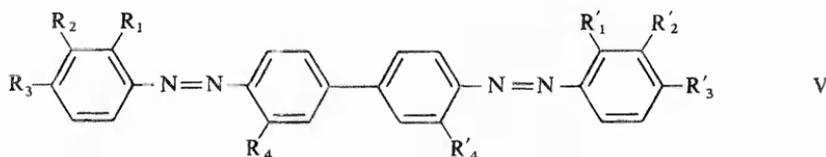
the polymer helix induces the formation of chiral dye associates but does not react itself with the dye<sup>37, 40</sup>. Models B to D represent some alternatives of sterically ordered polymer-dye adducts<sup>41</sup>. In these cases, the chromophoric groups are fixed in specific positions and are asymmetrically induced due to their chiral arrangement. Therefore, extrema of optical activity and Cotton effects should appear within the absorption range of the dyes, although the dye solutions are optically inactive. When adding an amylose solution (concentration  $\sim 2.3 \times 10^{-3}$  mol  $C_6H_{10}O_5$   $l^{-1}$ ) to an aqueous Congo red solution (concentration  $\sim 1.2 \times 10^{-4}$  mol  $l^{-1}$ ), the absorption spectrum changes only very little, but in the circular dichrogram several strong Cotton effects appear and the optical rotation differs widely from that of pure amylose<sup>42</sup>. Consequently, a chiral dye adduct is formed from amylose and Congo red. When plotting the circular dichroism  $\Delta\epsilon$  with constant amylose concentration as a function of the dye concentration, a typical saturation curve is obtained which may be described by a Langmuir isotherm<sup>39</sup>. Hence the equilibrium constant of the amylose-Congo red addition may be determined, which is  $K \sim 3 \times 10^4$  l mol<sup>-1</sup>. Moreover, a ratio of 15 glucose units to 1 Congo red molecule is reached at saturation.

The complex structure may also be determined from the  $\Delta\epsilon$  values according to the continuous variation method (JOB-method), and again a molar ratio of glucose:Congo red = 15:1 is obtained by this independent method.

The dissymmetry factor  $g_i = \Delta\epsilon/\epsilon$  is  $g_{515} = 2.6 \times 10^{-4}$  at the strongest induced Cotton effect ( $\lambda = 515$  nm) and thus much smaller than with the amylose-heavy metal complex ( $g = 10^{-3}$ – $10^{-2}$ ). Therefore, dye bonding cannot consist in the formation of an inherently dissymmetrical chelate complex.

It should be pointed out that this dye bonding is only possible with polysaccharides or cyclodextrines<sup>4,7</sup>. Linear oligosaccharides<sup>36</sup> or model compounds, as for example  $\alpha$ -methylglucoside or 4,6-ethylidene- $\alpha$ -methylglucoside, do not show any reaction with Congo red, either in the absorption spectrum or in the circular dichrogram. Consequently, there are specific bonding forces typical of polymers which, as well as sterical conditions, are necessary. In fact, these experiments do not reliably demonstrate the helix structure of the amylose in aqueous solution, but it is made probable that there are at least short ordered sections to which dye molecules may regularly add. According to our results, we prefer for these dye adducts model D where non-aggregated, single Congo red molecules are associated with ordered segments of the polymer.

Apparently, the dye molecules must also have a specific size and capacity to be able to add regularly to amylose. We, therefore examined 44 further dyes of different structure<sup>44</sup>. There were only 13 which formed chiral adducts with amylose showing induced Cotton effects. Their common characteristics are that each contains at least one azo group and is a direct dye for cotton. Ten of the dyes may be described by the general formula V:



The substituents, of course, are of importance for adduct formation. We were able to find rules for the kind and position of the necessary groups<sup>44</sup>. At any rate, the length of the dye molecules as well as the presence of at least two groups interacting with the amylose are probably important. In fact, dyes bearing all necessary functional substituents but having only half the length of the general formula do not form chiral adducts. Some examples of the Cotton effects between 400 and 600 nm are shown in *Figures 3 and 4*. The long-wave extrema always coincide with the longest-wave absorption bands. There are also several overlapped, positive and negative Cotton effects at 200 and 400 nm, but these cannot be clearly assigned to specific absorption bands.

It is emphasized that amylose and dye solutions alone do not show the slightest Cotton effect. The respective recording curves coincide with the baseline. For three other dye-amylose adducts (such as Benzoazurine G, Benzo Fast red F and Thiazine red R), the equilibrium constants  $K$ , the

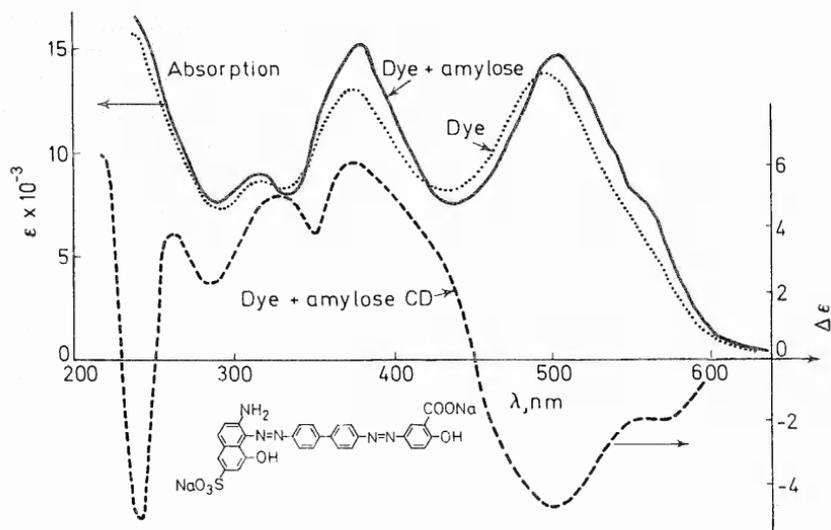


Figure 3. Absorption spectrum of Benzo Fast red F (...) and dye adduct with amylose (—); c.d. spectrum of dye-amylose adduct (---) in water ( $C_{\text{dye}} = 1.2 \times 10^{-4} \text{ mol l}^{-1}$ ; glucose:dye = 20:1)

Table 1. Data for the amylose adducts with some azo dyes

Name of dye	Number in Colour Index	Equilibrium constant $K \times 10^{-4}, \text{ l mol}^{-1}$	Dissymmetry factor $g \times 10^4$ (for wavelength $\lambda$ )	Ratio $\text{C}_6\text{H}_{10}\text{O}_5$ : dye for saturation
Congo red	22 120	$\sim 3$	2.6 (515 nm)	$\sim 15:1$
Benzo azurine G	24 140	3.9	1.5 (310 nm)	$\sim 42:1$
Benzo Fast red F	22 310	5.6	3.1 (500 nm)	$\sim 12:1$
Thiazine red R	14 780	6.0	0.3 (510 nm)	$\sim 7:1$

dissymmetry factors  $g$ , and the molar ratios at saturation were determined according to the above-mentioned methods<sup>44</sup> (see Table 1). In all cases,  $K$  is of the order of  $10^4 \text{ l mol}^{-1}$  similar to  $K$  for Congo red. The  $g$  values are very similar, too. Consequently, these are probably quite similar complexes. However, very different values are obtained for the molar ratios of glucose units to dye.

## DONOR-ACCEPTOR COMPLEXES WITH MACROMOLECULES

Donor-acceptor complexes are formed by combining an electron donating compound (D) with an electron accepting compound (A) according to the following equation<sup>45</sup>:



Complexes of this type, in which both components are low molecular weight

## COMPLEXES WITH POLYMERS AND MODELS

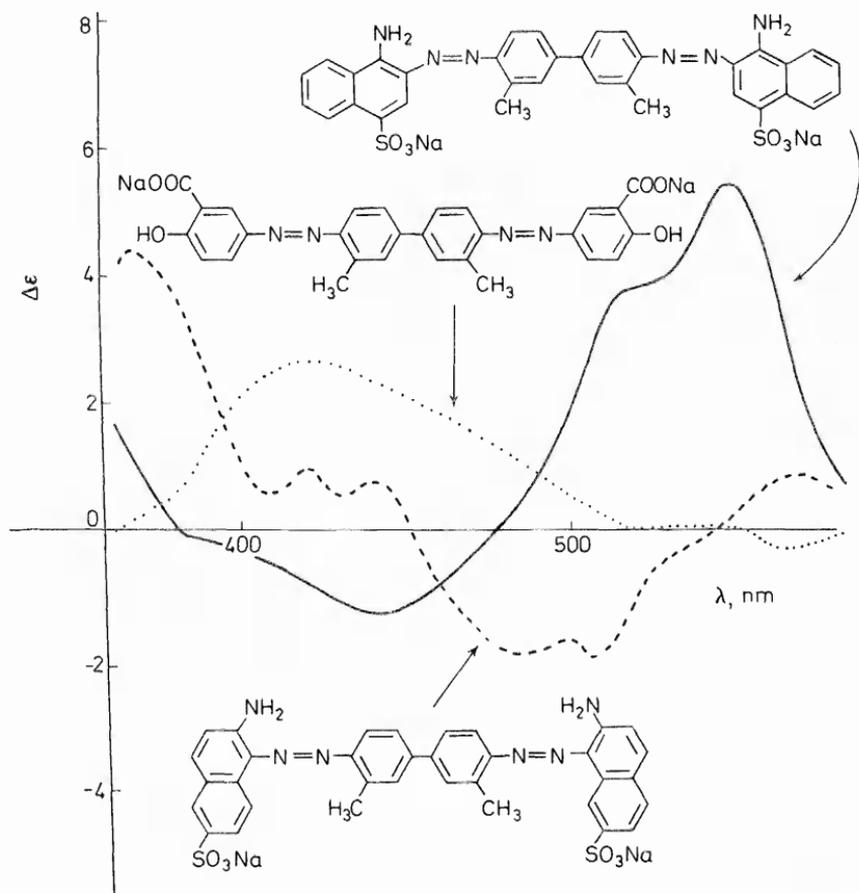
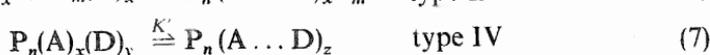
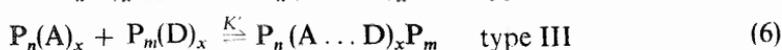
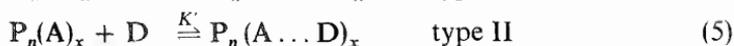
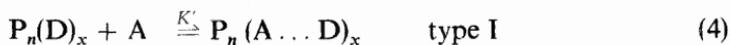


Figure 4. c.d. spectra of amylose adducts with benzopurpurin 4B (—), benzopurpurin 5B extra (---) or chrysamine (...) in water. ( $C_{\text{amylose}}: 2.4 \times 10^{-3}$  base mol  $l^{-1}$   $C_{\text{dye}}: 1.1 \times 10^{-4}$  mol  $l^{-1}$ )

compounds, have already been amply investigated. In recent years it has been recognized that such EDA complexes are also important in polymer science, for example, as initiators for polymerizations<sup>46</sup> or for producing alternating copolymers<sup>47</sup>.

The following explanations are limited to such EDA complexes, in which at least one of the components is a macromolecule. It is possible to distinguish four different types of complexes.

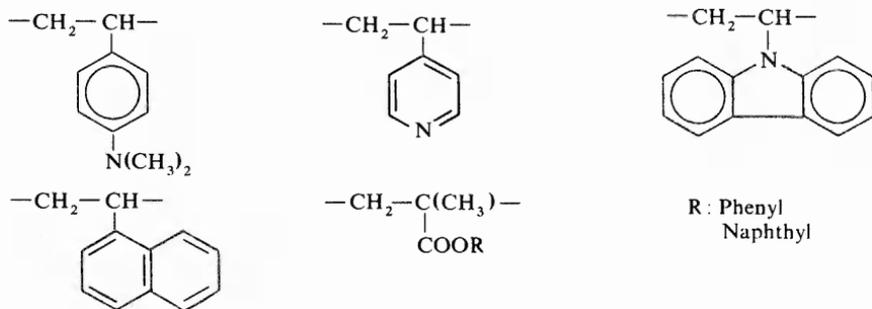


$P_n(A)_x$  and  $P_n(D)_x$  symbolize polymers with a large number ( $x$ ) of donor or

acceptor groups which are connected by covalences to the main chain. There are also other examples known in which A and D groups are found in the same macromolecule (type IV). Polymer EDA complexes have interesting properties and can, for example, be utilized as organic photoconductors in electrophotography<sup>48, 49</sup>. For this reason, many papers and patents have recently appeared in this area<sup>50-53, 58</sup>.

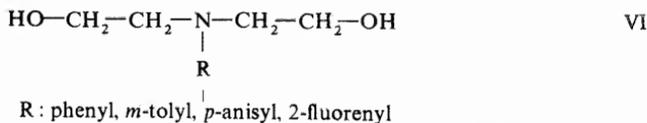
It has been shown that the c.t. bands in the absorption spectrum of polymer complexes are generally very similar to those of the low molecular weight model compounds. On the other hand, the equilibrium constants for complex formation in polymers and models are very different. In many cases, the constants are dependent upon the degree of polymerization, and upon the quantity and distribution of the complex-forming groups in the macromolecule as well as upon the tacticity. The reasons for such 'polymer effects'<sup>55</sup> have not yet been completely clarified. Of course it must be accepted that complex formation also causes a change in molecular shape and can eventually lead to crosslinking<sup>56, 57</sup>.

So far, the most widely examined complexes belong to type I, in which the donor groups are pendantly joined to the macromolecules and are complexed with low molecular weight acceptors. These polymers are in most cases obtained through radical or ionic polymerizations. Several examples

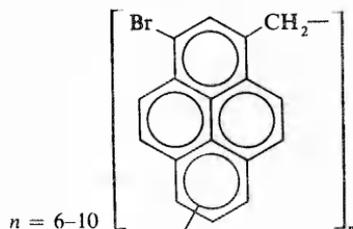


Scheme 4. Vinyl polymers with pendant donor groups (P(D))

of such polymer donors are presented in Scheme 4. Commonly used acceptors are shown in Scheme 5. There are also a number of donor polymers which are produced by means of polycondensation, for instance starting from the diols VI<sup>51</sup>.

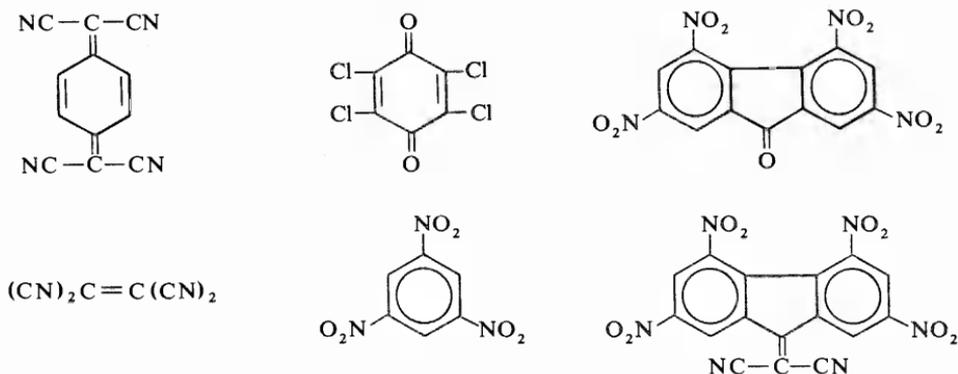


Of special interest is the product VII obtained through the polycondensation of monobromopyrene and formaldehyde, since it has many properties advantageous for use as electrophotographical material<sup>49</sup>.



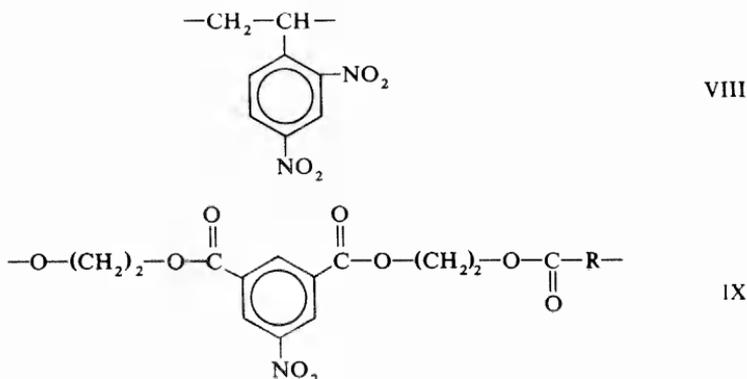
VII

In the case of bromopyrene resin, acceptors with especially high electron affinity were employed in order to shift the absorption bands in the long-wave area and to increase the light sensitivity (for instance tetranitrofluorenone or dicyanomethylene fluorene, see *Scheme 5*).



*Scheme 5.* Examples of low molecular acceptors

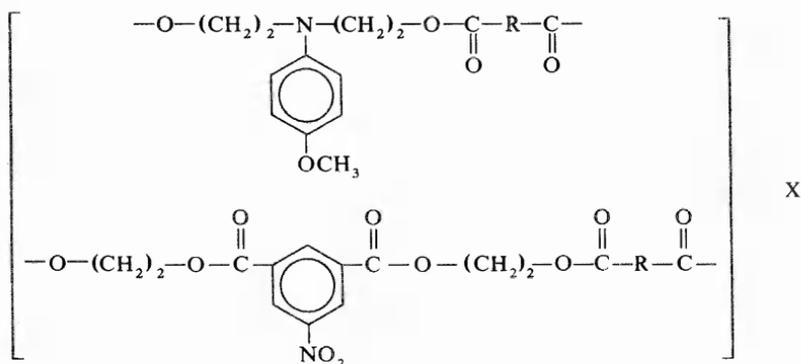
Polymer EDA complexes of type II have up to now been only slightly investigated. Two examples of polymers with acceptor groups are VIII<sup>59</sup> and IX<sup>51</sup>.



VIII

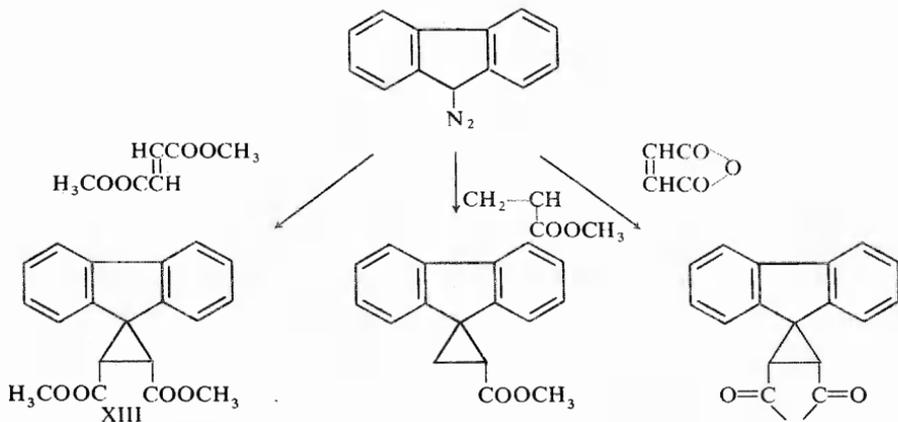
IX

By combining polymer donors with polymer acceptors, type III complexes are obtained<sup>51</sup>.



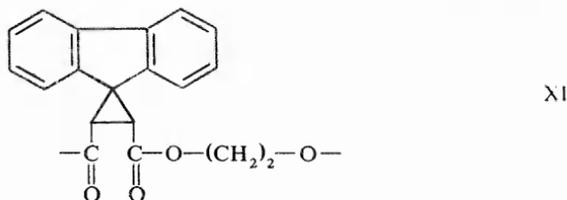
The most difficult to prepare are polymer EDA complexes which contain donors as well as acceptors in the same macromolecule<sup>51, 60</sup>.

Our own experiments with polymer EDA complexes are based upon the spirocyclopropanefluorene group. Appropriate starting material can be obtained through the reaction of diazofluorene with double bonds (Scheme 6).



Scheme 6. Synthesis of spirocyclopropane-1,9'-fluorene derivatives; starting materials for donor polyesters (P(D)) and models

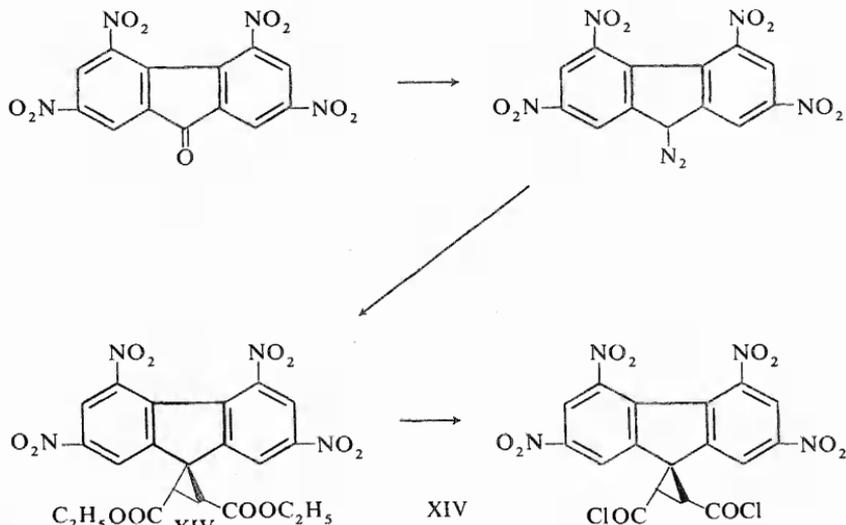
From this, various donor polyester and model compounds can be prepared (XI) which form coloured EDA complexes with TCNE or TCNQ as acceptors in dichloromethane.



It can be demonstrated that the equilibrium constant is dependent upon the degree of polymerization, and it is much higher for polyesters than it is

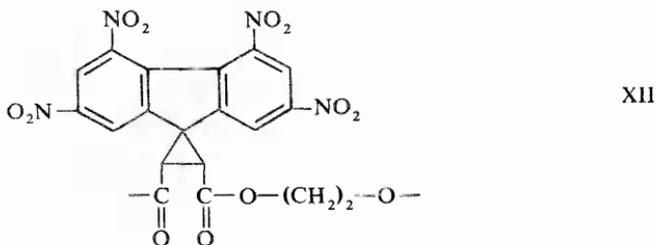
for the monomeric analogues. It is possible that sandwich-like EDA complexes are present because of the rigidity of the spirocyclic base units. This work has already been published in detail elsewhere<sup>61</sup>.

Acceptor polymers of analogous structure are obtained through the introduction of nitro groups in the spirocyclopropanefluorene system<sup>62</sup> according to *Scheme 7*.



*Scheme 7*. Synthesis of spirocyclopropane-1,9'-tetranitrofluorene derivatives; starting materials for acceptor polyesters (P(A)) and models

The starting material for this is tetranitrofluorenone. It is transformed into the diazo compound, which is reacted with diethyl fumarate. From this, the dicarbonyl chloride is prepared. A polyester is formed from this through polycondensation in solution with ethyleneglycol.

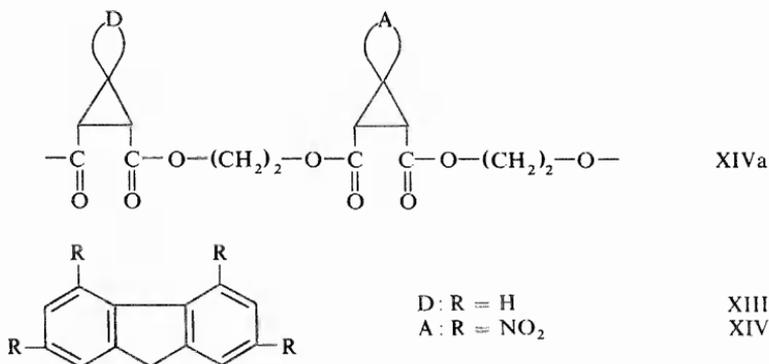


With fluorene as a donor, a type II EDA complex is formed. The absorption spectrum is very similar to that in the complex between the monomer spiroester and fluorene. In both cases, a c.t. band at  $\sim 400$  nm appears. The structure of both complexes may for that reason be the same. Nevertheless, the values for  $K\epsilon$  or for the equilibrium constant  $K$ , as determined by Benesi-Hildebrand-Scott, are here larger in the polymer complex than in the monomer model complex.

Table 2. Complex formation between fluorene (donor D) and acceptor polymer (P(A) XII) or acceptor model (A) (XIII)

P (A) XII + D				A + D		
$\lambda$ nm	$K\epsilon$ $\text{mol}^{-2} \text{l}^2 \text{cm}^{-1}$	$\epsilon$ $\text{mol}^{-1} \text{lcm}^{-1}$	$K$ $\text{mol}^{-1} \text{l}$	$K\epsilon$ $\text{mol}^{-2} \text{l}^2 \text{cm}^{-1}$	$\epsilon$ $\text{mol}^{-1} \text{lcm}^{-1}$	$K$ $\text{mol}^{-1} \text{l}$
410	603	600	1	462	1210	0.4
430	487	510	1	388	910	0.4
450	400	490	0.8	325	725	0.5

The acceptor polymer XII can also be complexed with the analogue donor polymer XI mentioned above<sup>62</sup>. This results in a type III complex. Although the spectrum indicates no distinct maxima, the broad absorption between 410 and 500 nm can certainly be attributed to complex formation since the individual components do not absorb in this area. A combination of the corresponding monomer acceptor XIV and donor XIII show a similar



spectrum. But even in this case, a constant is found for the polymer EDA complex which is clearly higher than for the corresponding monomer complex (see Table 3).

Table 3. Complex formation between P (D) XI and P (A) XII compared with model complexes

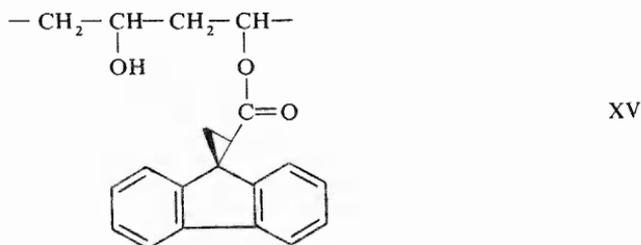
P (A) XII + P (D) XI				D XIII + A XIV		
$\lambda$ nm	$K\epsilon$ $\text{mol}^{-2} \text{l}^2 \text{cm}^{-1}$	$\epsilon$ $\text{mol}^{-1} \text{lcm}^{-1}$	$K$ $\text{mol}^{-1} \text{l}$	$K\epsilon$ $\text{mol}^{-2} \text{l}^2 \text{cm}^{-1}$	$\epsilon$ $\text{mol}^{-1} \text{lcm}^{-1}$	$K$ $\text{mol}^{-1} \text{l}$
410	2270	1436	1.6	400	700	0.6
450	1390	870	1.6	210	400	0.5

Starting from the dichlorides of the fluorene compound and of the tetra-nitrofluorene compound, a copolyester can be produced which contains donor as well as acceptor groups in the molecule and therefore belongs to type IV<sup>62</sup> (formula XIVa).

Copolyesters with D:A ratios of approximately 4:1 and 1.4:1 have been produced. During the synthesis, the reaction mixture attains an intense green-brown colour. The absorption spectrum of the polyester is distinctly different from the mixture of the monomer esters and also from the above-mentioned mixture of the donor and acceptor polyesters.

At 600–650 nm there appears a strong absorption band. The optical density of this band is strictly proportional to the concentration of acceptor groups in the solution. From this it can be concluded that these bands actually derive from intramolecular and not from intermolecular interactions between the donor and acceptor groups. By comparison with model compounds it can be estimated that in spite of intense colouration only about ten per cent of the groups available are complexed. The rigid fixation of the complexed groups by means of the spiran structure certainly plays a role in this particular type of polyester.

In conclusion, we have also produced polymers which carry a spirofluorene ring as a freely mobile side group on a polyvinylalcohol backbone, formula XV<sup>62</sup>.



The conversion lies between 35 and 60 mol per cent, depending upon the conditions. The modified polyvinylalcohol forms EDA complexes with TCNE and TCNQ. The c.t. bands show up at 555 nm or at 565 nm and agree with the low molecular weight model compounds. Presumably, the remaining OH groups of the PVA also play a role in the complex formation with polyesters, since the  $\xi_{k1}$  values, calculated by Liptay<sup>63</sup>, are not constant. Therefore only approximate values for  $K\varepsilon$  according to Benesi–Hildebrand–Scott can be calculated. Nevertheless it follows that in this case no polymer effect appears and the  $K\varepsilon$  values for polymer complexes and for models can be considered the same within the limits of experimental error.

## CONCLUSIONS

This short survey, with the help of several chosen examples, is meant to show that synthetic and naturally occurring macromolecules are capable of forming various types of adducts, complexes or chelates. Although mostly labile compounds are dealt with, many have properties of interest for scientific as well as practical reasons. In many cases the reactions take place only with macromolecules and are not possible with low molecular weight compounds or oligomers. Frequently a very specific secondary structure is also a prerequisite for complex formation. It is to be pointed out

that adduct formation with biopolymers certainly plays an important role in biological processes as well. Perhaps the experiments on synthetic polymers and model systems can contribute toward a better understanding of biochemical processes.

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