Polymer Bulletin 29, 119–126 (1992)

Polymer Bulletin

A new class of small band gap organic polymer conductors

E. E. Havinga[1,*], **W. ten Hoeve**[2], **and H. Wynberg**[2]

[1]Philips Research Laboratories, P.O. Box 80000, 5600 JA Eindhoven, The Netherlands
[2]Syncom b.v., Nyenborgh 4, 9747 AG Groningen, The Netherlands

Summary

Polysquaraines and polycroconaines have been synthesized. They form a new class of polymers with a small band gap, down to 0.5 eV. The small gap arises from the regular alternation of strong donor and acceptor-like moieties in a conjugated backbone.

Introduction

Conjugated organic polymers have intrinsic electronic semiconducting properties. They are, generally, characterized by rather large band gaps (1.5 to 4 eV (1)). Small band gaps are pursued because of their higher intrinsic (undoped) conductivity and they might give a clue for real intrinsically metallic organic polymers.

The discovery that the conjugated polymer poly(isothianaphthene), a modified polythiophene, has a small band gap of about 1.2 eV (2) started much theoretical work on the explanation of this phenomenon and suggestions for polymers with smaller band gaps (3). The basic idea behind this approach was that substituents inducing quinoid character in the ground state of the conjugated polymers tend to decrease the band gap. The best experimental result obtained along this line is a semiconductor with a band gap of 1 eV (4), and it is an open question whether smaller band gaps based on this principle can be realized or not. Polymers having much smaller band gaps are, however, very important because they would show high intrinsic conductivity (*i.e.* without doping), and, possibly, better transparency in the visible part of the spectrum.

---

[*] Corresponding author

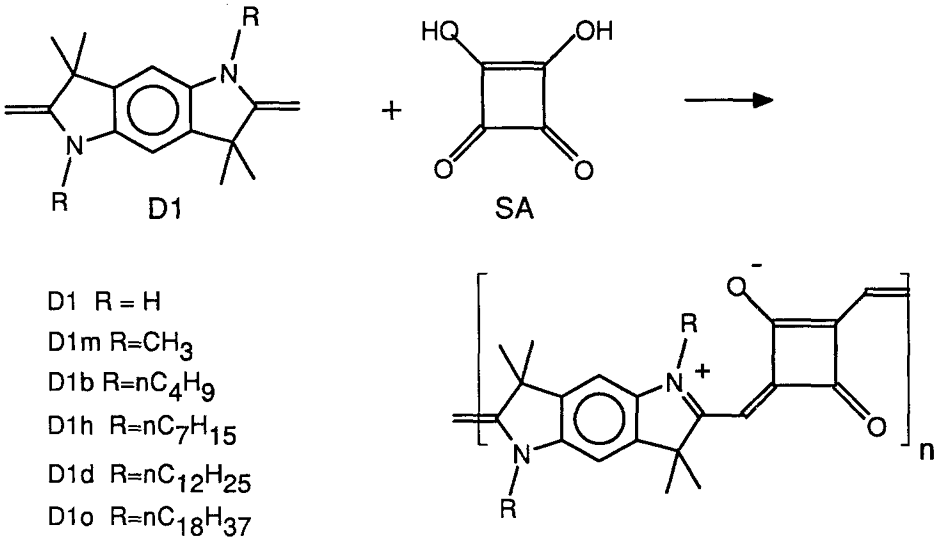
In this letter we report on a new class of polymers, polysquaraines and polycroconaines, in which the small band gap (down to 0.5 eV) arises from a different principle, *viz.* a regular alternation of strong donor and acceptor-like moieties in the conjugated back-bone. On the basis of the properties of a few representants of this class we will show that the principle works out quite successfully. Full details will be published shortly.

Concept of small-band-gap polymers

Our approach to small-band-gap polymers is based on the concept of a **regular alternation of conjugated strong donor and acceptor-like moieties in a conjugated back-bone.** If the HOMO levels of the donor and the LUMO levels of the acceptor moiety are close in energy the resulting band structure will show a small band gap. In fact one is changing the pseudopotential at the Fermi wave vector to lower values by chemical substitution.

In order to arrive at really small-band-gap conductors, **strong donors and acceptors** are needed. Strong donor-like moieties can be found in hetero ring systems with N, O or S atoms. Many of them show a large amount of delocalization of the positive charge in the rings. The main problem in realizing the alternate polymers lies in the acceptor moieties. We have now realized that squaric acid (SA) and croconic acid (CA), when incorporated in a polymer, are strong acceptors in which the negative charge is not completely localized on the O-atoms attached to the ring, but significantly delocalized in the chain. This follows from the properties of cyanine dyes, where these units can be inserted in the polyene chain connecting the donors to replace the anions without changing the colour appreciably (5,6). The polymers of these acids with bifunctional donor moieties constitute the new alternate polymers, polysquaraines and polycroconaines, respectively. Solubility in standard organic solvents can be obtained by substitution with side chains, *e.g.* alkyl groups.

It may be remarked that polymers with alternating **weak** donor and acceptor moieties do not show the wanted small band gap. This is illustrated by a recent experimental paper on the polymer of (2-thiophene)pyridine (7), which has a band gap that is only slightly smaller than that of polythiophene. No conductivity data were given.



D1

SA

D1 R = H

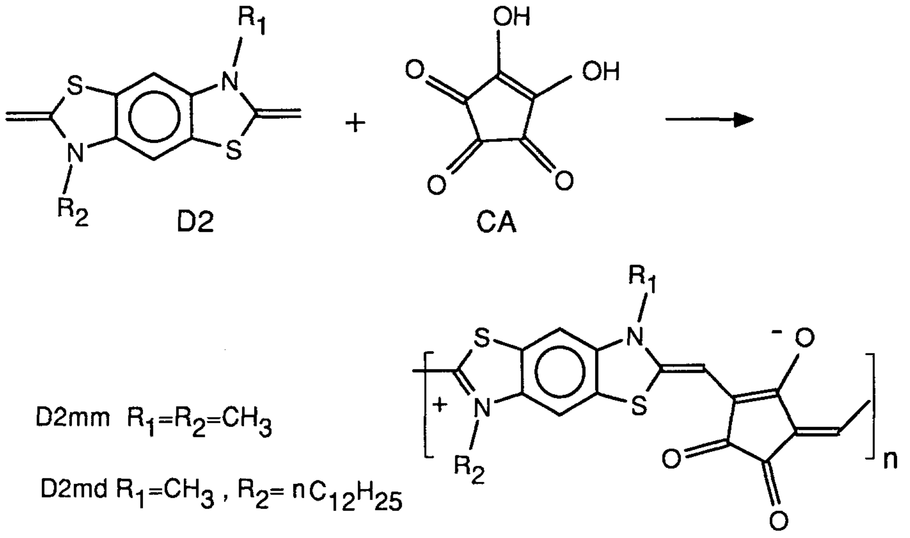
D1m R=CH_3

D1b R=nC_4H_9

D1h R=nC_7H_{15}

D1d R=$nC_{12}H_{25}$

D1o R=$nC_{18}H_{37}$



D2

CA

D2mm $R_1=R_2=CH_3$

D2md $R_1=CH_3$, $R_2= nC_{12}H_{25}$

Fig. 1. Condensation reactions of squaric acid (SA) with benzo (1,2-4,5) di(1-alkyl 2-methylene 3,3-dimethyl pyrroline), D1, (top) (b) of croconic acid (CA) with benzo (1,2-4,5) di (3-alkyl 2 methylene thiazole), D2 (bottom).

Experimental

The synthesis of the conjugated alternate donor-acceptor polymers can be carried out by a simple condensation reaction. Two representative examples are outlined in Fig. 1. Here the donors D1 and D2 are bifuctional analogues of well-known donors D′ in squaraine and croconaine dyes (5,6), see Fig. 2.

D1'   D2'

Fig. 2. Monofunctional donors benzo 1,2 (1-methyl 2-methylene 3,3-dimethyl pyrrolyne), D1′, and benzo 1,2 (3-alkyl 2-methylene thiazole), D2′.

The best procedure we found is to reflux both constituents in a higher saturated alcohol with catalyzing amounts of either a mineral acid (HCl, H_2SO_4) or a strong base (quinoline). In view of the instability of the donor D2 the reactions in this case were carried out starting from the, stable, HI salts.

The condensation reactions are very general. An overwhelming number of polymers $(\text{-SA-Dx-})_n$ and $(\text{-CA-Dx-})_n$ can be realized in this way. The acids condens easily with bifunctional donors carrying active H-atoms.In fact we have prepared a large number of polymers by this type of condensation with squaric acid or with croconic acid using aromatic diamines (*e.g.* *p*-phenylenediamine, thionin, 3,6-diaminoacridine), (substituted) terthienyls, azulene, neocuprine, *etc*.. These will be described elsewhere.

The polymers were characterized by FTIR, NIR-*vis*-UV spectra, DSC, conductivity and X-ray powder diffraction. For the more soluble polymers in addition GPC and ^1H-NMR data were obtained.

The IR and NMR data are in full accord with the expectations based on data of dyes (D′-A-D′) of the acids condensed with two monofunctional donors. The absence of IR absorptions in the region 1680 - 1840 cm^{-1} in the SA polymers confirms the

1,3-substitution scheme (8). DMSO was unsatisfactory as a reaction medium because of the occurrence of mixed 1,2- and 1,3- substitutions.

The polymers are rather intractable and insoluble because of the rigid, conjugated, main chains. Solubility can be increased by the introduction of alkyl, alkoxyl, etc. side chains, a well known procedure for conjugated polymers. In this way we arrived at slightly soluble polymers (between 0.5 g and 5 g per l chloroform) for (-SA-D1b-)$_n$, (-SA-D2md-)$_n$ and (-CA-D1d-)$_n$, and (-SA-D1h-)$_n$, (-SA-D1d-)$_n$ and (SA-D1o-)$_n$ were even better soluble than that. X-ray diffraction data point to varying amounts of crystallinity of the samples. No clear picture of the dependence on chemical structure could yet been found.

GPC of (-SA-D1h-)$_n$ and (-SA-D1d-)$_n$ gives molar masses corresponding to 15 and 25 units (-SA-D1-), respectively, using polystyrene as a standard. The degree of polymerization of the other, less soluble, polymers will probably be somewhat less. Namely, the polymerization reaction is terminated when the polymer precipitates from the reaction solution. From our work on oligothiophenes (9) it is known that some 15 to 25 pairs of alternate bonds (-C=C-) are sufficient to approach the polymeric properties of band gap and conductivity very closely. For the molar masses measured this condition is amply fulfilled.

The *vis*-NIR absorption spectra of solutions of the polymers in chloroform are similar to those of the dyes (D′-A-D′), referred to above, except for a marked red shift and a slight broadening. In the solid state, measured on thin cast films or on suspension in paraffin oil or nujol, the red shift is larger and the broadening towards the infrared side is increased. For a few polymers (-A-D-)$_n$ and corresponding dyes (D′-A-D′) the values of the energy of the absorption maximum as well as of the absorption cut-off (band gap) of the solid state polymer is given in Table 1. All spectra are virtually independent of the length of the alkyl substituent on the nitrogen. We found that both for polysquaraines and for polycroconaines the band gap tends to decrease with increasing strength of the donors. The smaller band gaps E_g , down to 0.5 eV, are found for the CA polymers. This reflects the greater acceptor strength of CA compared to that of SA (7). Poly (CA-D1) shows an unexpected large band gap, possibly because of steric crowding preventing planar configurations. An alternative explanation could be that we only succeeded in getting oligomers having a rather low molar mass (the samples are very crystalline). All polymers are slightly green-blue due to a satellite peak at higher energies, which is also present in the dyes (D′-A-D′).

Table 1. Conductivity σ (S/cm) and energy levels (eV) from *vis*-NIR absorption measurements for two polysquaraines and two polycroconaines. E_g denotes the band gap (cut-off) of the solid state, and E_{max} the energy at absorption maximum in the solid state (*s*) and in chloroform solution ,(*l*) , respectively. For comparison literature data (6) on spectra of corresponding dyes (D′-A-D′) in methylenechloride solution are also given.

Acid	Donor	σ (S/cm)	E_g	$E_{max}(s)$	$E_{max}(l)$	$E_{max}(l)$	Donor′
SA	D1d	10^{-7}	1.15	1.35	1.45	1.96	D′2b
SA	D2md	10^{-7}	0.8	1.25	1.50	1.85	D′3m
CA	D1d	10^{-9}	1.2	1.35	1.50	1.60	D′2b
CA	D2md	10^{-5}	0.5	0.9	1.35	1.58	D′3m

The polymers as such are stable in air at room temperature, and many of them can be heated up to 300 °C in air without any observable degradation. The chloroform solutions, however, deteriorate upon standing in air and daylight. Under these circumstances the polymers degrade to oligomers. This is manifest both from GPC data, where a large number of maxima at lower molar masses are found, and from *vis* absorption spectra, where the original spectrum gradually fades out and up to 5 maxima appear at higher energies, with that of the corresponding low-molecular dye as upper limit. Assignment of the various peaks to definite oligomers has not yet succeeded. However, this observation fortifies the interpretation of the NIR absorption maxima as band-to-band transitions and discounts an identification with polaron band transitions,

The conductivity of the polymers has been measured with the usual four-probe method on *virgin* samples, *viz.* pressed bars of about 20x5x1 mm^3 (insoluble polymers) and/or thin cast layers on glass of about 20x5x0.001 mm^3 (soluble polymers). Some data are shown in Table 1. The use of virgin samples does not necessarily imply that the polymers are completely undoped. Namely, accidental doping either by unintended impurities or by oxidation in air might very well occur. In fact, many samples showed a gradual increase by one or two orders of magnitude in conductivity upon standing in air for some days. For this reason the values of σ listed are the minimum values found immediately after preparation of the samples.

On the other hand, a simple estimate of expected intrinsic conductivities σ at room temperature by the standard equation $\sigma = n_e.e.\mu$ with $n_e = n_o \exp(-E_g/2kT)$, assuming a number of electrons in the conduction band $n_o = 10^{22}$ cm^{-3} and a mobility $\mu \simeq 10^{-5}$ cm^{2}V^{-1}s^{-1} (actually the sum of electron and hole mobilities) gives values of $\sigma \simeq 10^{-6}$, 8.10^{-9} and 6.10^{-11} S/cm for band-gap values of 0.5, 0.75 and 1.0 eV, respectively. It is, hence, very likely that, at least in some of the polymers, the measured conductivities are close to intrinsic values. The additional extrinsic conductivity is p-type.

Exposing solid samples to the vapour of iodine at 70 °C immediately increases the conductivity. Values of σ vary between 10^{-3} and 1 S/cm for heavily doped samples. Values around 1 S/cm are also found for thin cast layers in which the dopant DDQ (2,3-dichloro 4,5-dicyanobenzoquinone) has been included in the solution. Such high values of conductivity point clearly to throughconjugated systems.

The ground state of the undoped polymers is degenerate, just like that of polyacetylene. In lightly doped materials one would expect, therefore, soliton-like behaviour on the part of the charge carriers.

Conclusions

From the results obtained with these polymers it is clear that the principle of inducing smaller band gaps into conjugated polymers by a regular alternation of donor and acceptor moieties works quite well. The band gap is smallest for a combination in which the electronegativity difference between donor and acceptor is greatest. Factors that counteract the decrease in band gap are steric hindrance preventing a completely planar configuration and the limited conjugation in both the donor and the acid rings. Both factors tend to decrease the width of the conduction and valence bands. Investigations aiming at smaller band gaps by using still stronger donors and/or by decreasing steric hindrance are underway. Furthermore, we are testing some ideas about other donors and acceptors that are more fully conjugated. Whether the limit of an intrinsic-metallic conjugated polymer can actually be realized along these lines is still an open question.

Acknowledgement. Thanks are due to A. Pomp for technical assistance.

References

1. Bredas JL (1989) in *Handbook of Conducting Polymers,* Skotheim TA, ed., Marcel Dekker Inc., New York-Basel Chapter 25.
2. Wudl F, Kobayashi M, Heeger AJ (1984) *J.Org. Chem.* **49** 3381-3384.
3. *e.g.* Bredas JL (1987) *Synth. Met.* **17** 115-121;
   Kertesz M, Lee YS (1989) *Synth. Met.* **28** C545-C522.
4. Ikenoue Y, Wudl F, Heeger AJ (1991) *Synth. Met.* **40** 1-12.
5. Fabian J, Hartmann H (1980) *Light Absorption of Organic Colorants* (Reactivity and Structure Concepts in Organic Chemistry, Vol. 12) , Springer Verlag, Berlin-Heidelberg-New York, p. 191.
6. Yasui S, Matsuoka M, Kitao T (1988) *Dyes and Pigments* **10** 13-22.
7. Zhou ZH, Maruyama T, Kanbara T, Ikeda T, Uchimura K, Yamamoto T, Tokuda K (1991) *J. Chem. Soc., Chem. Commun.* **1991** 1210-1212.
8. Manecke G, Gauger J (1969) *Makromol. Chem.* **125** 231-246;
   Green BR, Neuse EW (1973) *Polymer* **14** 230-231;
   Neuse EW, Green BR (1974) *Polymer* **15** 339-345.
9. Havinga EE, Rotte I, Meijer EW, ten Hoeve W, Wynberg H (1991) *Synthetic Metals* **41-43** 473-478
   Havinga EE, Rotte I (1992) *Mol.Cryst.Liq.Cryst., paper accepted.*

Accepted July 13, 1992 C