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SYNTHESIS AND COMPLEX FORMATION OF MACROMOLECULES HAVING TETRATHIOFULVALENE STRUCTURE

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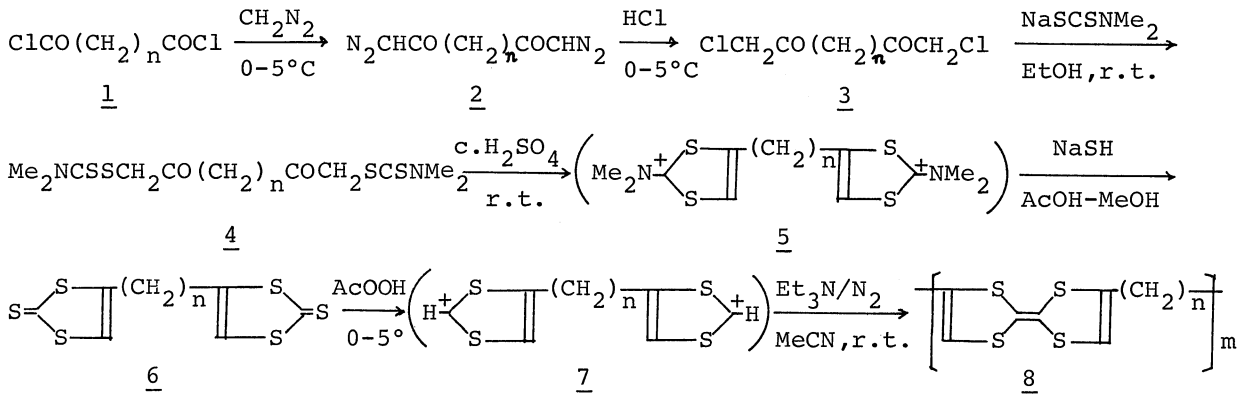
The new polymer containing tetrathiofulvalene (TTF) structure was synthesized by coupling of polymethylene-bis-4-(1,3-dithiole-2-thione) with base and charge transfer (CT) complex formation of them with tetracyano-p-quinodimethane (TCNQ) and 2,3-dichloro-5,6--dicyano-p-benzoquinone (DDQ) was examined.

Recently, much interest has been shown in the field of highly conducting organic CT complexes. The most attractive system is the salt of TTF and TCNQ, which displays one of the highest conductivity (ca. 500-350 $\Omega^{-1}cm^{-1}$ at room temperature) reported to date for an organic CT salt. Thus, new synthetic methods of TTF derivatives have been studied by several groups of workers[1]. We have also reported convenient methods of synthesizing the intermediates for TTF and the formation of CT complex of TTFs[2]. It is desirable, however, to devise the synthesis of macromolecules containing TTF structure (and complex with TCNQ) for utilizing such organic compounds as a component of electro-conducting materials. This communication describes our attempt to synthesize a polymer containing TTF structure in the main chain and its complex with some acceptors.

In our study, 2-2 coupling method of 1,3-dithiole-2-thione was used to make up macromolecules. For the joint of two dithiole-rings, $-(CH_2)_n-$ chain was selected to prevent the decrease of solubility and donating character of the polymer. For framing 1,3-dithiole-2-thione structure, acidic ring closure reaction was employed (4→5). The synthetic route is shown in Scheme 1.

Bis-(β-ketochloride) (3) was prepared from corresponding acid chloride (1)

Scheme 1



via diazoketone (2) in good yield according to the procedure of E.Fahr[3]. Chloride (3) was converted to bis-dithiocarbamate (4) by reaction with two molar sodium N,N-dimethyldithiocarbamate in ethanol at room temperature for 2 hr (Table 1). Dithiocarbamate (4) was carefully dissolved in conc. sulfuric acid(5-10 fold by wt.) at room temperature and kept at 50° for 10 min to perform the cyclization to 5[4] and followed by addition of acetic acid, methanol and a large excess of sodium hydrosulfide successively. The reaction mixture was poured into water to precipitate yellow solid of bis-(1,3-dithiole-2-thione) (6) quantitatively. IR and UV of 6 (recrystallized from chloroform) were shown in Table 1, indicating a good accordance with those of 1,3-dithiole-2-thione itself. If necessary, bis-(1,3-dithiolium salt) (5) (e.g. n=4,2BPh_4^-: $\nu_{C=\overset{+}{N}}$ 1600cm^{-1}, λ_{max} in H_2SO_4,245,303nm) could be isolated as an intermediate adding an aqueous solution of sodium tetraphenylborate to the sulfuric acid solution. This 5 also gave bis-thione 6 quantitatively by treating with sodium hydrosulfide similarly. The structure of bis-thione 6 was also proved from the NMR data: e.g.n=3 (in $CDCl_3$) 2.00(qui,2H, J=7Hz),2.76(t,4H,J=7Hz), 6.70(s,2H) ppm.

Table 1 Bis-dithiocarbamates (4) and Bis-thiones (6)*

n	4 yield %	4 mp °C	4 IR(KBr) cm^{-1}	4 UV (λ_{max}^{EtOH}) nm	6 yield %	6 mp °C	6 IR(KBr) cm^{-1}	6 UV ($\lambda_{max}^{CH_2Cl_2}$) nm
3	85	132-3	1720,1490	246,277	~100	101-4	1050,1025	236,376
4	80	134-5	1720,1490	247,278	~100	184-5	1050,1030	236,375

*Elemental analyses of 4 and 6 are consisted with calculated value.

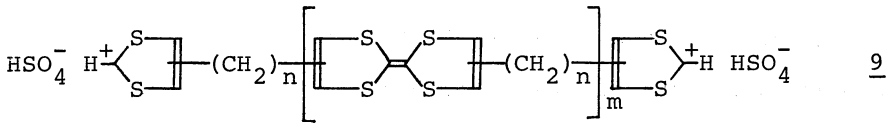
To a solution of bis-thione (6) in methylene chloride, was added a excess amount of 20%-acetic acid solution of peracetic acid at 0-5° and stirred for 1.5 hr. After adding perchloric acid and methanol, the reaction mixture was

poured into ether to precipitate a salt, bis-1,3-dithiole-2-ylium perchlorate (7, unidentified).[5] To a suspension of 7 in acetonitrile, was added excess triethylamine at room temperature under a nitrogen atmosphere. The color of solution turned to green rapidly. After 1 hr, the solid was filtered and washed with water and methanol successively. The greenish-brown powders (8) thus obtained decompose at ca. 170° and are insoluble in common solvents. The polymer was analyzed after repeated extraction with hot acetonitrile to remove presumable cyclic oligomers of low molecular weight. The results are shown in Table 2, together with IR[6] and UV[7] data of TTF, indicating that the polymer contains expected structure unit.

Table 2. Physical properties of TTF-polymer 8

n	yield %	IR(KBr) cm^{-1}	UV nm (λ_{max}^{MeCN})	C % Found (Calcd)	H % Found (Calcd)	m	MW
3	40	800,770,745	300,325	42.16(44.27)	3.47(3.30)	15	4100
4	45	795,775,745	295,324	43.95(46.52)	4.25(3.90)	12	3550
TTF		797,781,735	303,317*	*in cyclohexane			

Rather large differences in carbon content from the calculated value (based on repeated unit) would be ascribed to the irregular terminal structure in polymer chain of low molecular weight. Assuming the most probable terminal structure as 9, the molecular weight was calculated to be about 3500-4000 as shown in Table 2.



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Finally, the polymer (8) was refluxed in acetonitrile with an equimolar amount of TCNQ or DDQ under a nitrogen atmosphere. After washing with acetonitrile repeatedly, the powdery complexes, 10 and 11, were analyzed. IR and UV data and the ratios of polymers to acceptors calculated from N contents were summarized in Table 3.

UV data of 11 could not be available because of its complete insolubility. However, the absorption at 745-743 and 840-837 nm for 10 in dilute acetonitrile solution is corresponding to that of $TCNQ^{\cdot-}$[8]. IR data indicate that both 10 and 11 show the existence of characteristic absorption at $\nu_{C\equiv N}$ regions. The complex 11 also shows the absorption of aryl group obserbed in TTFs-DDQ complexes at 1560-1570 cm^{-1} as well as disappearence of carbonyl band around 1680cm^{-1} for DDQ.[2]

Table 3. CT complexes of polymer (8) with TCNQ and DDQ

	n	decomp.(°C)	m:1*	IR(KBr)cm^{-1}
TCNQ complexes (10)	3	212-215	6:1	2220
	4	237-238	6:1	2220
DDQ complexes (11)	3	>300	5:3	2250, 1560
	4	>300	2:1	2250, 1570

* Ratio of TTF unit to acceptor (mol:mol)

The formation of 1:1 adduct could not be achieved on the whole for both cases probably due to the lack of solubility of polymer 8 and product, 10 or 11 in reaction media. A heterogeneous reaction, however, may prevent the penetration of the acceptor into the insoluble polymer particle so that the complexation seems to be restricted only on the surface of the polymer. Thus, the formation of 1:1 adduct might be expected at least on the surface layer of the products, 10 and 11.

Further studies on physical properties such as electroconductivity and ESR will be reported elsewhere.

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