Polymer Bulletin 8, 87-93 (1982)

Polymer Bulletin

Chemical Stability of 7,7',8,8'-Tetracyanoquinodimethane Salts with Polycations Containing Sulfur Atoms in the Main Chain

J. Pecherz and M. Kryszewski

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences,
PL-90-364 Łódź, Poland

SUMMARY

Storage and chemical stability of TCNQ anion radical salts with polycations containing sulfur atoms in the main chain was investigated as a function of time and solvent used for their synthesis. The UV and visible light absorption spectra of solution have evidenced that the storage of these polymeric salts at room temperature results in the appearance of a new absorption band asscribed to α,α-dicyano-p-toluoylcyanide anion. It was found that the ageing reaction depends on the residual solvent as well as on the method of synthesis of these complex salts.

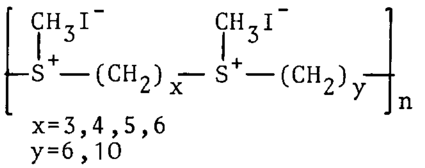
INTRODUCTION

Complex salts of 7,7',8,8'-tetracyanoquinodimethane (TCNQ) with polycations are known semiconducting polymers (KRYSZEWSKI 1980, LUPINSKI et al 1967). Due to their high conductivity they have attracted a lot of attention also from the view point of practical applications. In the latter case their chemical and storage stability are of particular importance. Several papers were devoted to the studies on chemical and electrical stability of TCNQ salt with many polycations (MIZOGUCHI et al 1978, KRYSZEWSKI et al 1981, CIESIELSKI et al 1979, SZERLE et al 1974, VARAKINA et al 1981).
It was found that the increase of specific resistivity of these compounds and the course of their ageing is related to the formation of α,α-dicyano-p-toluoylcyanide anion (MIZOGUCHI et al 1978, KRYSZEWSKI et al 1981). The aim of this work is to investigate the stability of TCNQ salt with polycations containing sulfur atoms in the backbone chain in order to analyse the influence of solvent and method of synthesis as well as of the composition of the complexes on their stability and electrical properties.

EXPERIMENTAL

Synthesis of TCNQ complex salts with sulfur atoms in the main chain was carried out using the method described in our previous paper (PECHERZ et al 1981). The results of elemental analysis have shown a compleate substitution of iodine anions by anion radicals $TCNQ^{\overline{\cdot}}$. The structure and denotations of polycations used for prepared complex salts are given below:

0170-0839/82/0008/0087/$01.40

structure	abbr.
 $\left[-\overset{\overset{CH_3I^-}{\vert}}{S^+}-(CH_2)_x-\overset{\overset{CH_3I^-}{\vert}}{S^+}-(CH_2)_y- \right]_n$ x=3,4,5,6 y=6,10	$K_s[x,y]$ $K_s[3,6]$; $K_s[4,6]$ $K_s[5,6]$; $K_s[6,6]$ $K_s[3,10]$; $K_s[4,10]$ $K_s[5,10]$; $K_s[6,10]$

UV-and visible light absorption spectra for the complexes of TCNQ salts were obtained with a Unicam SP-1700 spectrometer using 10^{-5} mol/l solutions of the complexes in acetonitryle (ACL) and N,N'-dimethylformamide (DMF). Electrical properties of stored samples were determined on the similar way like in previous papers (PECHERZ et al 1981, PECHERZ, KRYSZEWSKI, in press).

RESULTS AND DISCUSSION

Fig.1. shows the changes of resistivity ρ in function of time for the complex $K_s[4,6]$ with various contents of neutral $TCNQ^o$ in the solid state. The increase of resistivity is very distinct only for simple salt $K'_s[4,6]_o$ while for complex salts these changes after a year of storage in air are small.

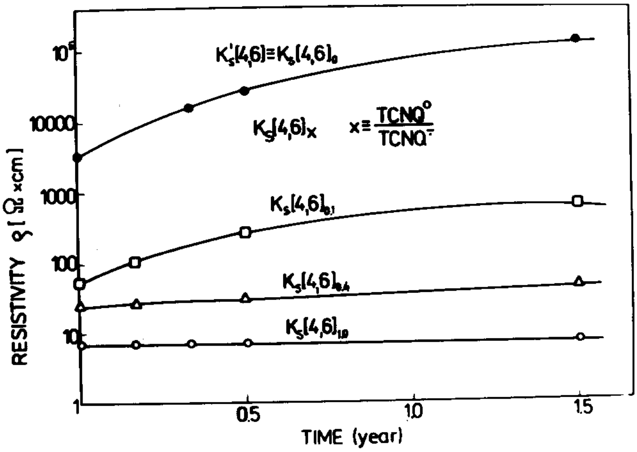


Fig.1. The dependence of resistivity ρ of $K_s[4,6]$ in function of storage time in air

This behaviour is similar to this observed for other polymeric salts of TCNQ (MIZOGUCHI et al 1978, KRYSZEWSKI et al 1981). The storage time does not influence the resistivity and the main features of the absorption spectra of all complexes $K_s[x,6]$ with the ratio $TCNQ^o/TCNQ^{\cdot-}=1$, where x=3,4,5,6. It should be noted that for complexes $K_s[x,10]$, where x=3,4,5,6, as well as for complexes $K_s[x,6]$ with the ratio $TCNQ^o/TCNQ^{\cdot-} < 0.8$ the absorption spectra show an appearance of a new band at λ=480nm corresponding to α,α-dicyano-p-toluoylcyanide anion. The intensity of this band is low which indicates the structural changes are very slow. The above described behaviour suggested that it may be related to the method of synthesis of these complex salts. For $K_s[4,6]$ complex obtained by one stage method (CIESIELSKI, KRYSZEWSKI, 1976) for which $TCNQ^o/TCNQ^{\cdot-}=1$ no changes in absorption spectra could be detected during a year of storage while for the same complex with the same composition but obtained by the two stage method (REMBAUM et al 1969) the storage time in similar conditions results in the appearance of absorption at λ=480 nm (Fig.2). In one stage method the solvent used consisted of acetonitryle (ACL) and ethanol (4:1 by volume). The precipitated complex was washed out with hot ACL, cold ACL and then with methanol and ether followed by drying in vaccum at 40°C. The removal of the remaining solvents was rather easy because of their high volatility. In the two stage method (REMBAUM et al 1969) the synthesis of the complex salts occurs in DMF or in N,N'-dimethylacetamide (DMAA). The removal of the traces of solvent in this case is difficult because of the high boiling points of these solvents ($t_{b,DMF}=153^oC$ $t_{b,DMAA}=165^oC$). This conclusion also was pointed out in the other work (VARAKINA et al 1981) in which the investigated polymeric salts were obtained in DMAA. The traces of the solvent were found still after drying at 140°C. This results makes possible to suggest that the main reason for the lack of chemical stability of $K_s[4,6]$ and of other complex salts obtained by two stage method using DMF and DMAA are the traces of remaining solvent. In fact it was found for the complex $K_s[4,6]$ obtained by two stage method that careful washing out at first with methanol and then with hot and cold ACL and once again with methanol and ether resulted, after drying in vaccum at 40°C, in a quite stable material.

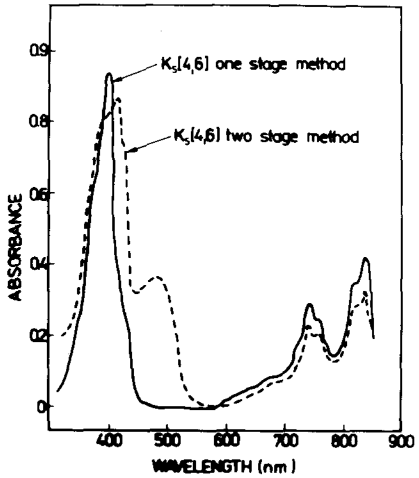


Fig.2. Changes in visible absorption spectra of $K_s[4,6]$ complex salts with time. Complexes were prepared by one and two stage methods

It does not show absorption change after three months storage in air and after heating for several days at 60°C.
The investigations of electron spectra changes of complexes $K_s[4,6]$ in DMF and ACL solutions evidenced an important influence of these solvents on the stability of these complexes. It follows from Fig.3 that DMF causes a rapid changes in absorption spectrum of the $K_s[4,6]$ complex leading to the formation of α,α-dicyano-p-toluoylcyanide anion. This effect is due to a fast decomplexation of the complex into its components. The interactions between $TCNQ^{0}$ and $TCNQ^{\bar{\cdot}}$ molecules are only very weak thus they accelerate the formation of α,α-dicyano-p-toluoylcyanide anion. In ACL solutions no absorption change could be detected after 3 months storage of $K_s[4,6]$ complex solution. It suggests that a strong interaction between $TCNQ^{0}$ and $TCNQ^{\bar{\cdot}}$ occurs.
The absorption spectrum of $K_s[4,6]$ complex, for which the ratio $TCNQ^{0}/TCNQ^{\bar{\cdot}}$ was 0.4 and 0.1 shows, in ACL, only a very weak absorption at λ=480 nm as compared with analogous absorption in DMF.

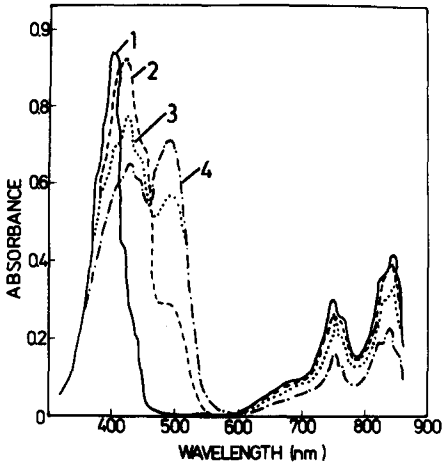
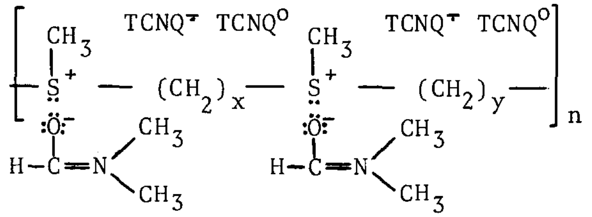
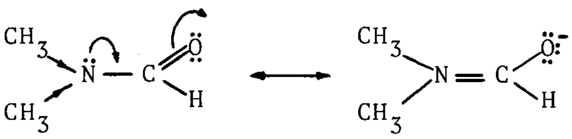


Fig.3. Change of visible absorption spectra of $K_s[4,6]$ complex salt with time in DMF solution after: 1-0 hr; 2-4 hr; 3-16 hr; 4-48 hr

The question on the reason for fast decomposition of complexes under study in DMF and DMMA can be answered considering the structure of DMF and DMMA molecules as well as their interacions with S^{+} atoms in polycation chain (and not only with TCNQ molecules):

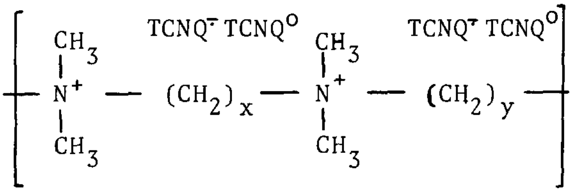




and analogically for DMAA solutions.

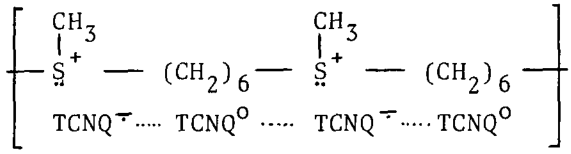
Electron affinity of oxygen atom to sulfur atom with lone electron pair is greater than this of nitrogen atom in DMF molecule to sulfur atom in polycation chain. These interactions of solvent molecules with polycations of low concentration (about 10^{-5} mol/l) cause an association of polycations and a decrease of interactions between $\mathrm{TCNQ}^{\bar{\cdot}}$ and S^+. This results in decomplexation of complexes. If it should be the case thus the decomposition of TCNQ complexes with polycations containing S^+ atoms in the bacbone chain must be faster as compared with polycations containing N^+ atoms in polycation chain.

The affinity of DMF or DMAA molecules to nitrogen atoms in polycations is smaller than this discussed before, because of the lack of electron pair at nitrogen atom in ammonium salt and because the steric hindrance connected with two methylen groups at N^+ atom:



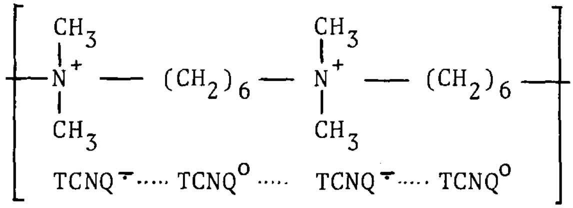
$$\left[-\underset{CH_3}{\overset{CH_3}{N^+}} - \overset{\mathrm{TCNQ}^{\bar{\cdot}}\,\mathrm{TCNQ}^{0}}{(CH_2)_x} - \underset{CH_3}{\overset{CH_3}{N^+}} - \overset{\mathrm{TCNQ}^{\bar{\cdot}}\,\mathrm{TCNQ}^{0}}{(CH_2)_y} - \right]_n$$

This suggestion was confirmed by experiments. The changes absorption rate of the DMF solutions of complexes:



$$\left[-\overset{CH_3}{\ddot{S}^+} - (CH_2)_6 - \overset{CH_3}{\ddot{S}^+} - (CH_2)_6 - \atop \mathrm{TCNQ}^{\bar{\cdot}} \cdots \mathrm{TCNQ}^{0} \cdots \mathrm{TCNQ}^{\bar{\cdot}} \cdots \mathrm{TCNQ}^{0} \right]_n$$

$K_s[6,6]$



$$\left[-\underset{CH_3}{\overset{CH_3}{N^+}} - (CH_2)_6 - \underset{CH_3}{\overset{CH_3}{N^+}} - (CH_2)_6 - \atop \mathrm{TCNQ}^{\bar{\cdot}} \cdots \mathrm{TCNQ}^{0} \cdots \mathrm{TCNQ}^{\bar{\cdot}} \cdots \mathrm{TCNQ}^{0} \right]_n$$

$K\,[6,6]$

as a function of time are presented in Fig.4. The rates of absorption increase at $\lambda=480$ nm are faster for $K_s[6,6]$ than for $K[6,6]$ complexes, but finally this reaction leads in both cases to a complete complex decomposition and to the formation of α,α -dicyano-p-toluoylcyanide anion like it was found before (MIZOGUCHI et al 1978, KRYSZEWSKI et al 1981).

Such changes of absorption have not been found for the complexes with $\mathrm{TCNQ}^{0}/\mathrm{TCNQ}^{\bar{\cdot}} = 1.0$ in ACL. It seems that an important conclusion can be drawn: one stage method of the synthesis of these complexes without the use of DMF and DMAA (the solvent used is ACL/ethanol 4:1) (CIESIELSKI, KRYSZEWSKI 1976) leads to stable complex salts of this type.

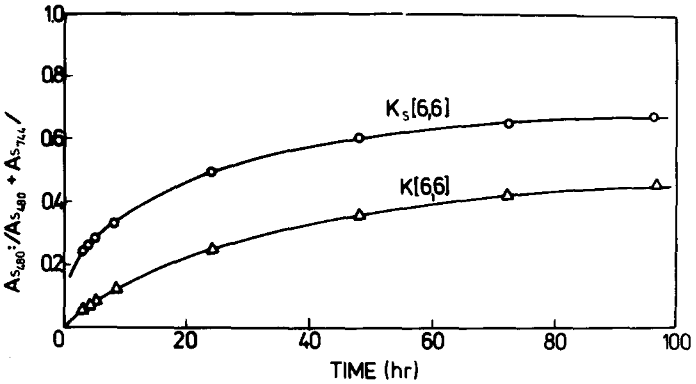


Fig.4. Change in $As_{480}/(As_{480} + As_{744})$ as function of time in DMF solutions of complexes $K_s[6,6]$ (o) and K [6,6] (▲)

All reactions described in the discussion of synthesis conditions of TCNQ complex salts (KRYSZEWSKI et al 1981) also occur in preparation of TCNQ complex salts with polycations containing S^+ atoms including chemical changes leading to the formation α,α-dicyano-p-toluoylcyanide anion. These reactions in the presence of water can be discussed in terms of acid-base equilibria and of the active role of hydroxyl anions. On should also take into consideration the part of $TCNQ^0$ in the formation of α,α-dicyano-p-toluoylcyanide anion. The concentration of hydroxyl anions can be higher than this calculated from the value of water dissociation constant, because in these cases the protolysis of a strong conjugated base $TCNQ^{\dot{-}}$ results in formation of a weak conjugated acid H_2TCNQ with a low dissociation constant (KRYSZEWSKI et al 1981).

In the case of TCNQ complex salts with polycations containing sulfur atoms in the main chain, for which $TCNQ^0/TCNQ^{\dot{-}} = 1$, the above mentioned hydrolysis reactions do not occur because of much lower basicity of the conjugated base $TCNQ^{\dot{-}}$ existing in the complex, as compared with the basicity of $TCNQ^{\dot{-}}$ in simple TCNQ salts. This observation is valid provided that the decomplexation occuring in DMF or DMAA can be neglected.

Strong interactions between $TCNQ^{\dot{-}}$ and $TCNQ^0$ in complex salts of TCNQ result in a decrease of the basicity of $TCNQ^{\dot{-}}$ anions which leads to a decrease of their protolysis reaction. TCNQ complex salts for which $TCNQ^0/TCNQ^{\dot{-}} \ll 1$ undergo a hydrolitic reaction all the more the lower is this ratio in agreement with the results shown in Fig.1. The water content in these complexes in the solid state depends on their hydroscopicity (KRYSZEWSKI et al 1981). Complex salts of TCNQ containing nonsubstituted anions are transformed according to the above discussed reaction all the more the higher is the contents of halogen anions. The presence of these species results in the inhomogeneity of $TCNQ^{0}$ and $TCNQ^{-}$ distribution and in consequence in the increase of basicity of $TCNQ^{-}$. Elemental analysis of the complex TCNQ salts of polycations with S^{+} atoms shows that the halogen atoms are completely substituted thus their chemical stability is high as compared with these salts in which the concentration of halogen anions is higher. This is the reason why the complexes described before (VARKINA et al 1981) are less stable independently of contents traces of solvent molecules. It shall also be mentioned that the lack of chemical stability of the complex salts investigated in previous works is the ratio $TCNQ^{0}/TCNQ^{-} \ll 1$.

CONCLUSIONS

The studies on chemical stability of TCNQ salts with polycations containing S^{+} atoms in the main chain lead to the following conclusions. Chemical stability of these complex salts is higher when: i) the ratio $TCNQ^{0}/TCNQ^{-}$ is closer to unity; ii) the substitution of halogens is more complete and when. iii) the residue of solvent used in the synthesis like DMF or DMAA is very low.

One stage method of synthesis used in the preparation of the complex under study (CIESIELSKI et al 1976) seems to be the most useful in fulfilling all these conditions.

REFERENCES

KRYSZEWSKI, M.: Semiconducting Polymers PWN- Polish Scientific Publishers, Warsaw, 1980
LUPINSKI, J.H., KOPPLE, K.D., HERTZ, J.J.: J.Pol.Sci., 16, 1561 (1967)
MIZOGUCHI, K., TSUJI, S., TSUCHIDA, E., and SHINOHARA, J.: J.Polymer Sci., Polymer Chem.Ed., 16, 3259 (1978)
KRYSZEWSKI, M., CIESIELSKI, W., and PECHERZ, J.: Acta Polymerica, 32, 524 (1981)
CIESIELSKI, W., PECHERZ, J., and KRYSZEWSKI, M.: VII International Microsymposium Polycondensation processes, Łódź, Poland, March 27-29, 1979
SZERLE, A.I., et al : Vysokomol. Soed. A16, 2051 (1974)
VARAKINA, E.N., et al :Vysokomol. Soed., B10, 640 (1981)
PECHERZ, J., CIESIELSKI, W. and KRYSZEWSKI, M.: Macromolecules, 14, 1139 (1981)
PECHERZ, J. and KRYSZEWSKI, M.: Acta Polymerica, in press
CIESIELSKI, W. and KRYSZEWSKI, M.: Ann.Soc.Chim. Polonorum, 50, 947 (1976)
REMBAUM, A., HERMANN, A.J., STEWART, F.E. and GUTMAN, F.: J.Phys.Chem., 73, 513 (1969)

Received August 9, accepted August 1o, 1982