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COPOLYMERIZATION OF SCHIFF BASES WITH TETRACYANOETHYLENE

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ABSTRACT

The copolymerization of four Schiff bases (substituted benzylidene anilines) with tetracyanoethylene has been investigated. The reaction takes place in the absence of an initiator through a zwitterionic mechanism, leading to copolymers with an almost alternating structure. When dimethylformamide was used as solvent, a concurrent radical homopolymerization of tetracyanoethylene with the formation of an azoporphyrin structure occurs.

INTRODUCTION

Tetracyanoethylene (TCNE) is a strong acceptor of electrons, and it forms charge transfer complexes (CTC) with a large variety of donors. If the donor contains polymerizable bonds, then TCNE may initiate its homopolymerization or may copolymerize with it. Simionescu et al. [1–3] reported the spontaneous copolymerization of TCNE with 2-oxazolines substituted in position 2 with electrono-donating groups such as 2-(β -N-carbazolyethyl)-2-oxazoline and 2-(9-anthrylethyl)-2-oxazoline. The actual starting step involves the transfer of an electron from the oxazoline ring (n -type donor) to TCNE (π -type acceptor).

There are a few reports [4, 5] of the polymerization of Schiff bases which are electron donors of the n -type containing heterogeneous double bonds. Their alternating co-oligomerization with compounds having

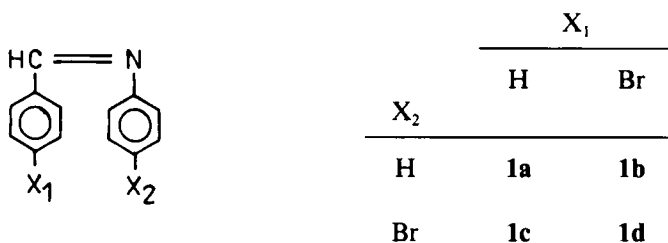
electrophilic reactivity (i.e., acrylic acid, succinic anhydride, or haloacrylic acids) has also been reported [6, 7]. To our knowledge, no references exist on the encatennation of Schiff bases initiated by TCNE.

The copolymerization of some Schiff bases with TCNE and the characterization of copolymers formed are reported below.

EXPERIMENTAL

Materials

Schiff bases submitted to copolymerization (**1a-1d**) were synthesized by refluxing benzaldehyde and *p*-bromobenzaldehyde in alcohol (ethanol) with aniline or *p*-bromoaniline. The crystalline products were separated and purified by recrystallization from ethanol, and their structures were confirmed by elemental analysis and ¹H NMR.



TCNE (Fluka) was recrystallized from benzene and purified twice by sublimation just before use.

The solvents were dried and purified by the usual methods.

Polymerization

The copolymerizations were carried out in sealed glass ampules in an inert atmosphere (argon). The polymers were separated by precipitation in anhydrous diethyl ether. After filtration, the solid product was dried *in vacuo* at 60°C.

Polymer Characterization

The IR (KBr pellets) and ¹H-NMR (dimethyl-*d*₆-sulfoxide) spectra were recorded by using Perkin-Elmer 577 and JEOL C60 HL (60 MHz) spectrophotometers, respectively. The electronic spectra were registered by using a Unicam SP 800B spectrometer.

The compositions of the copolymers were established by elemental analysis (nitrogen and bromine). Thermogravimetric data were obtained by using a Paulik-Paulik-Erdey (Budapest) thermobalance with a heating rate of 12°/min.

RESULTS AND DISCUSSION

When solutions of *N*-benzylidene anilines are mixed with TCNE, a yellow-greenish donor-acceptor complex is formed. It appears in the electronic spectrum at a specific absorption which is not present in the electronic spectra of individual monomers. By using the Job method of continuous variation [8], it has been established by UV spectroscopy (solvent, CH₂Cl₂) that the ratio of donor/acceptor in the complex is 1:1. In the course of time, or on heating, the color of the solution changes to red. The electronic spectra recorded in acetonitrile and methylene chloride for an equimolar mixture of comonomers exhibits continuous absorptions with maxima at 320 and 386 nm, respectively, which are attributed to CTC formed in the first stage (Fig. 1). Moreover, a new

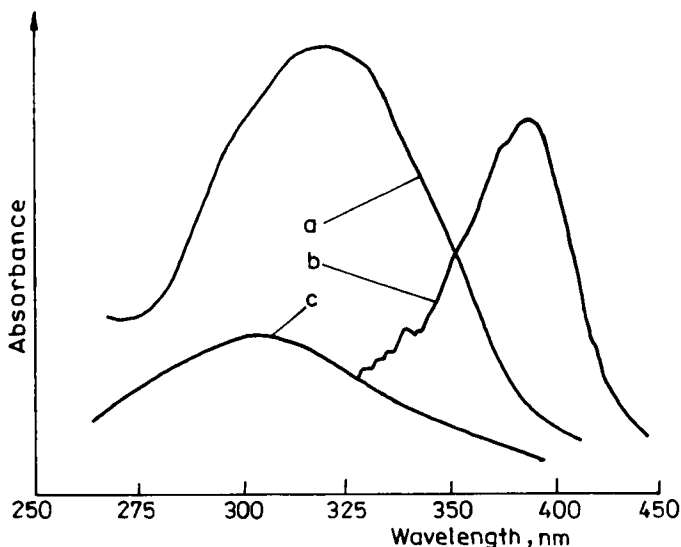
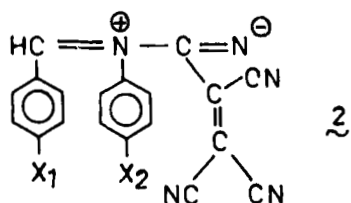
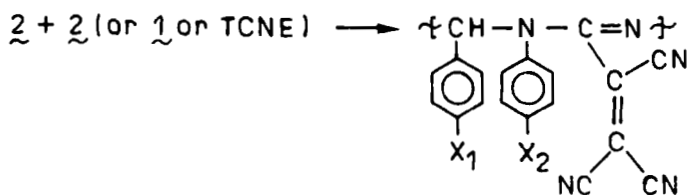


FIG. 1. UV spectra of TCNE-1a (molar ratio 1:1) in acetonitrile (a) and CH₂Cl₂ (b); pure TCNE in DMF (c).

absorption can be seen in the visible domain, extending to 600 nm (Fig. 2). It does not have a fine vibrational structure and its intensity increases with temperature. Comparison between experimental data and that reported in the literature on the TCNE anion (TCNE⁻) [9, 10] suggests that the maximum in the visible domain corresponds to a zwitterion of the type



This zwitterion, which is assumed to originate from the donor-acceptor complex by electron transfer from the iminic nitrogen to the acceptor, is the active species in both the initiation and the propagation reactions:



The proposed mechanism of copolymerization is supported by the

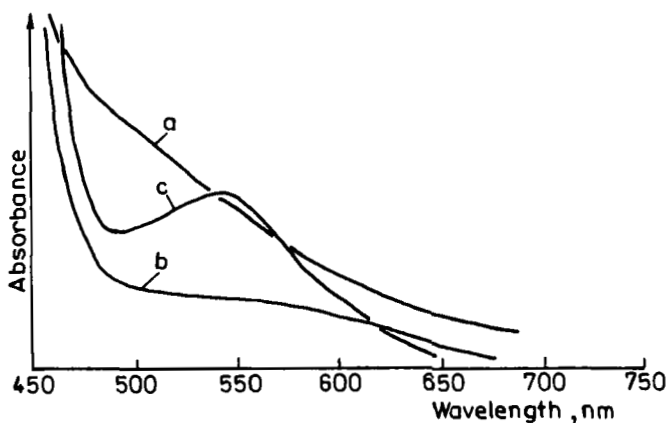


FIG. 2. Visible spectra of TCNE-1a (molar ratio 1:1) in acetonitrile (a) and CH₂Cl₂ (b); pure TCNE in DMF (c).

dependence of conversion and the composition of the reaction products on 1) the position of halogen in the phenylic ring of the Schiff base, 2) the polarity of solvents, and 3) the feed composition.

Thus, since the presence of bromine in the phenylic ring, which is adjacent to a nitrogen atom, determines a decrease of its electron density and lowers the polarization of the iminic bond, the tendency toward formation of the zwitterion is decreased. Therefore, the addition of free TCNE to the macrozwitterions is favored, and the copolymer composition is richer in TCNE (Table 1).

On the other hand, the presence of bromine in the benzylidenic ring does not seriously influence the yield and the composition of copolymers since the halogen is too distant to affect the electronic density of iminic nitrogen.

The polarity of solvents determines the formation and stability of zwitterions, i.e., the higher the dielectric constant, the higher the conversion (Table 2).

The deviation registered in the case of DMF may be explained by the capacity of this polar solvent to form a CTC with TCNE [10]. The effect of this competitive side reaction is reflected in the dramatic decrease of conversion.

The electronic spectrum of the CTC of DMF and TCNE has a maximum at 310 nm, and the complex dissociates upon heating, giving rise to the anion radical TCNE⁻ (Figs. 1 and 2).

The fact that maximum yields were obtained for an equimolar feed composition (1:1) of Schiff bases:TCNE and the alternating structure of

TABLE 1. The Influence of Substituents on the Copolymerization of Schiff Bases with TCNE^a

Sample	Schiff base	F_2^b	f_2^c	N, %	Br, %	Yield, %
1	1a	0.5	0.48	21.9	—	69.0
2	1b	0.5	0.45	16.56	21.85	70.3
3	1c	0.5	0.56	19.54	17.97	48.6
4	1d	0.5	0.62	18.03	27.63	47.8

^aPolymerization conditions: [1] + [TCNE] = 4.4 mol/L, temperature = 112°C, time = 24 h, solvent = DMF.

^b F_2 is the mole fraction of TCNE in the feed.

^c f_2 is the mole fraction of TCNE in the copolymer.

TABLE 2. The Influence of the Nature of the Solvent on the Copolymerization of Schiff Base (1a) with TCNE^a

Sample	Solvent			N, %	Yield, %	
	Type	Dielectric constant, ϵ	F_2^b			
5	Benzene	2.28	0.5	0.53	23.66	28.0
6	Acetonitrile	3.90	0.5	0.51	22.97	31.9
7	DMF	3.82	0.5	0.48	21.9	5.9
8	Nitrobenzene	36	0.5	0.49	22.2	33.4

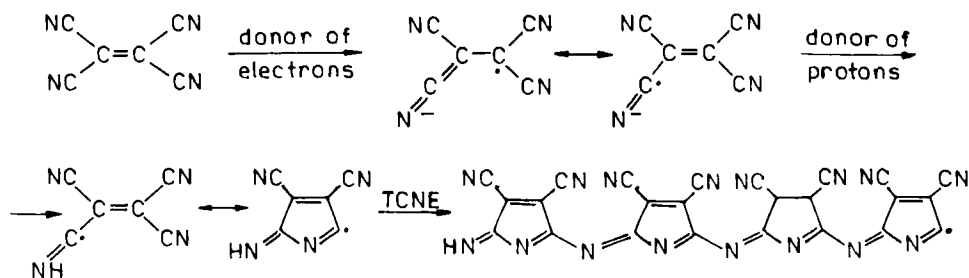
^aPolymerization conditions: [1a] + [TCNE] = 4.4 mol/L, temperature = 75°C, time = 24 h.

^b F_2 = mole fraction of TCNE in the feed.

^c f_2 = mole fraction of TCNE in the copolymer.

copolymers also supports the zwitterionic mechanism proposed for this copolymerization (Table 3). Exceptions may be seen when DMF was used as the solvent: the yield increased with the TCNE content in the feed and the copolymerization diagram is practically azeotropic. The reason might be the thermal dissociation of the DMF-TCNE complex followed by homopolymerization of TCNE, or the participation of more than one nitrile group of the same TCNE molecule in copolymerization.

Thermal polymerization of TCNE at rather high temperatures (200°C), in the presence of amides was reported by Berlin and Matveeva [11]. However, at temperatures higher than 110°C the polymerization of TCNE in DMF occurs without any other donor. The process can be described according to the mechanism proposed by Wöhrle [12]:



In the reactions shown above, the role of both donor of electrons and

TABLE 3. The Influence of Feed Composition on the Copolymerization of Schiff Bases with TCNE^a

Sample	Solvent	F_2^b	Temperature, °C	N, %	f_2^c	Yield, %	Solubility
9	Acetonitrile	0.96	75	—	—	0.0	
10		0.75		26.0	0.59	6.9	CHCl ₃ , acetone, benzene
11		0.66		22.93	0.51	12.5	THF, acetonitrile
12		0.50		22.97	0.51	16.2	DMF, DMSO
13		0.33		22.50	0.49	15.1	DMF, DMSO
14		0.25		22.12	0.48	9.1	
15		0.04		—	—	0.8	
16	Benzene	0.66	75	—	—	23.5	THF, benzene
17		0.50		23.6	0.53	32.2	Acetone
18		0.33		—	—	25.6	
19	DMF	0.95	112	35.55	0.83	83.5	DMF, DMSO
20		0.75		30.8	0.70	73.6	DMF, DMSO
21		0.67		26.54	0.61	65.7	DMF, DMSO
22		0.50		21.90	0.48	64.5	DMF, DMSO, THF
23		0.33		19.18	0.40	29.8	THF, acetone
24		0.25		14.96	0.26	18.6	THF, acetone
25		0.14		—	—	2.2	CHCl ₃

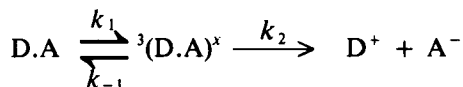
^aPolymerization conditions: time = 24 h, total concentration of [1a] + [TCNE] = 4.4 mol/L with the exception of Experiments 9–15 when it was 2.2 mol/L.

^b F_2 = mole fraction of TCNE in the feed.

^c f_2 = mole fraction of TCNE in the copolymer.

donor of protons is played by DMF. This mechanism is supported by several facts.

a) *The formation of CTC (DMF-TCNE) and its capacity to dissociate thermally in ions [10]:*



The process is enhanced by light, and the ion-radicals TCNE^- generated are very stable both in the absence and the presence of atmospheric oxygen.

b) *The influence of radical retarders or inhibitors (Table 4).* No polymer is formed from TCNE when DMF (Samples 19 and 26) is replaced by acetonitrile (Sample 9) or nitrobenzene (Sample 27). The presence of the latter, in addition to DMF, causes a drop in TCNE conversion in the homopolymer (Sample 28). On the other hand, the copolymerization of TCNE with Schiff bases, which involves a zwitterionic species, proceeds with maximum yields in nitrobenzene due to its high polarity (Table 2).

The addition of hydroquinone in the copolymerization of TCNE with **1a** in DMF causes an increase in the reaction yield (compare Samples 31 and 22), and the hydroquinone is inserted in the polymer structure (Sample 33). The explanation may lie in the polymerization of nitrile groups initiated by aminic groups $-\text{NH}$ formed through a proton transfer from hydroquinone to TCNE. The NMR spectra of polymers have a signal at 7.94 ppm, corresponding to phenylic protons from hydroquinone (Fig. 3). At the same time, the aminic groups formed through proton transfer are indicated in the IR spectra by an augmentation of absorbance at $2700\text{--}3500\text{ cm}^{-1}$ (Fig. 4). On the other hand, the addition of anthraquinone in the copolymerization of TCNE with **1a** in benzene has a slight influence on the polymer yield (compare Samples 32 and 17).

c) *The Properties of the polymers obtained* as governed by synthesis conditions. For example, the solubility decreases with an increase of TCNE content in the polymers, and the color darkens from beige to anthracite black with greater conjugation.

The thermal stability of polymers obtained in DMF increases as the content of TCNE in the copolymer decreases. A weight loss of $\sim 10\%$ up to 200°C is associated with the removal of acceptor and evaporation of solvent traces. At higher temperatures ($> 300^\circ\text{C}$) of cyclization, cross-

TABLE 4. The Influence of Radicalic Inhibitors on the Homo- and Copolymerization of TCNE

Sample	Monomer	Monomer concentration, mol/L	Solvent	Temperature, °C	Time, h	Inhibitor	Yield, %
26	TCNE	5.8	DMF	120	3	—	11.3
27	TCNE	5.8	nitrobenzene	120	3	nitrobenzene	0.0
28	TCNE	5.8	DMF: nitrobenzene 1:1 vol/vol	120	3	nitrobenzene	4.3
29	TCNE	5.8	DMF	120	24	—	49.6
30	1a + TCNE 1:100 mol/mol	5.8	DMF	120	24	—	90.2
31	1a + TCNE 1:1 mol/mol	4.4	DMF	112	24	hydroquinone ^a	84.4
32	1a + TCNE 1:1 mol/mol	4.4	benzene	75	24	anthraquinone ^b	23.7
33	1a + TCNE 1:10 mol/mol	4.4	DMF	112	24	hydroquinone ^a	128.7

^a40% based on monomers weight.^b4% based on monomers weight.

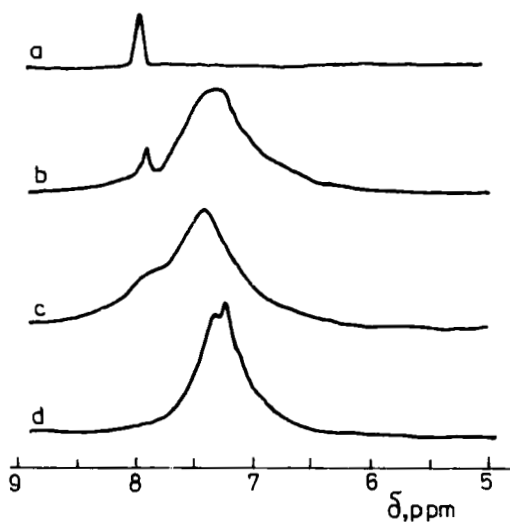


FIG. 3. $^1\text{H-NMR}$ spectra of poly(TCNE-co-Schiff base): (a) Sample 33, (b) Sample 31, (c) Sample 20, and (d) Sample 24. Solvent, $\text{DMSO-}d_6$; reference, TMS.

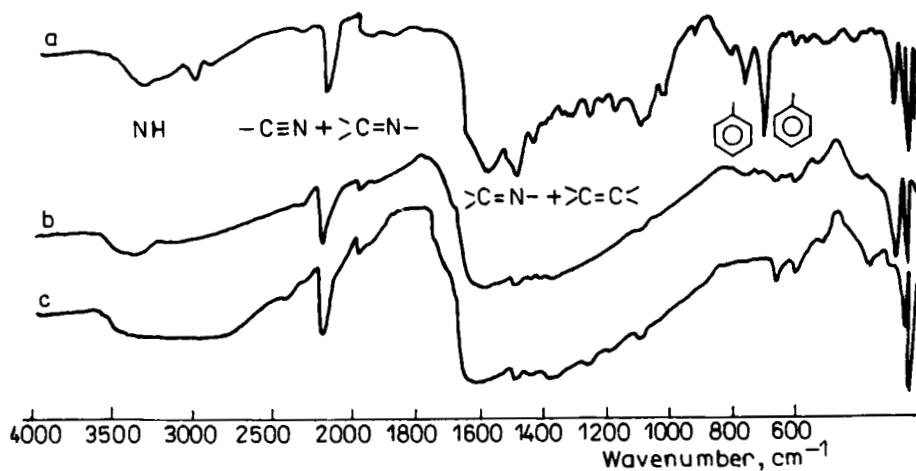


FIG. 4. IR (KBr pellets) of TCNE-Schiff base copolymers: (a) Sample 24, (b) Sample 19, and (c) Sample 31.

linking and destruction processes may occur (Fig. 5). The rather higher stability of copolymers with a lower content of TCNE units may be explained by the ability of free nitrile groups to give rise to thermally resistant tridimensional networks. The intermolecular reactions of nitrile groups with azoporphyrin structures (i.e., TCNE homopolymers) are less favored.

The semi- and photoconductivity of copolymers are under investigation and will be reported elsewhere.

CONCLUSIONS

1. Schiff bases can react spontaneously with TCNE through a zwitterionic mechanism to form copolymers of almost alternating structure.
2. A competitive ion-radical homopolymerization of TCNE with the

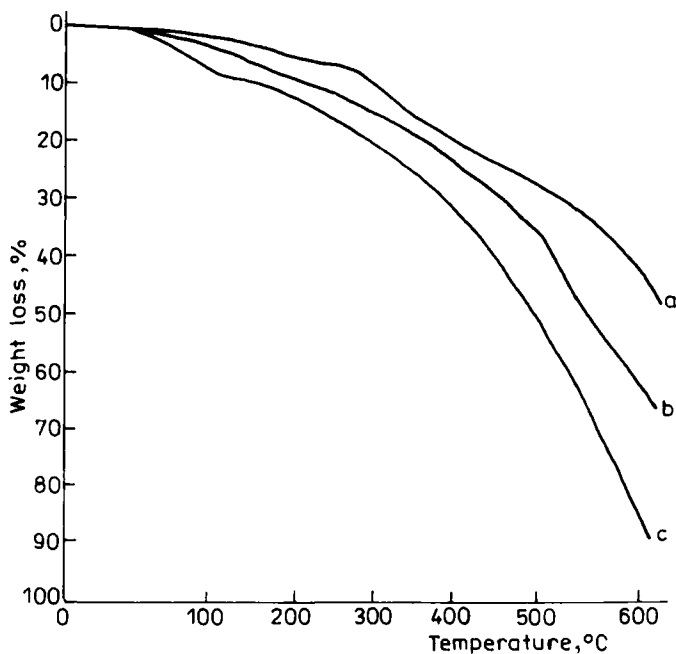


FIG. 5. Thermal degradation of polymers derived from TCNE and Schiff bases: (a) Sample 24, (b) Sample 22, and (c) Sample 19.

formation of azoporphyrin structures occurs in DMF, which provides both the necessary electrons and protons.

REFERENCES

- [1] C. I. Simionescu, G. David, and M. Grigoras, *Eur. Polym. J.*, **23**, 689 (1987).
- [2] G. David, M. Grigoras, and C. I. Simionescu, *Ibid.*, **24**, 347 (1988).
- [3] C. I. Simionescu, G. David, and M. Grigoras, *Ibid.*, **24**, 849 (1988).
- [4] P. Fenuti, G. Audisio, G. Cottica, and A. Fere, *J. Polym. Sci., Polym. Lett. Ed.*, **12**, 451 (1974).
- [5] K. Harada, Y. Mizoe, J. Furukawa, and S. Yamashita, *Makromol. Chem.*, **132**, 269 (1970).
- [6] T. Saegusa, S. Kobayashi, and J. Furukawa, *Macromolecules*, **8**, 703 (1975).
- [7] T. Balakrishnan and M. Perigasamy, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1885 (1982).
- [8] P. Job, *Ann. Chim. (Paris)*, **9**, 113 (1928).
- [9] O. W. Webster, W. Mahles, and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3678 (1962).
- [10] N. Kushibiki and H. Yoshida, *Bull. Chem. Soc. Jpn.*, **50**, 349 (1977).
- [11] A. A. Berlin and N. G. Matveeva, *Dokl. Akad. Nauk SSR*, **140**, 368 (1961).
- [12] D. Wöhrle, *Adv. Polym. Sci.*, **10**, 35 (1972).