

## Polycondensation of N-Methyl Carbazole with Dihalogenomethane and some Properties of the Polymer

Almeria Natansohn

Department of Plastics Research, Weizmann Institute of Science, Rehovot, Israel

**Dedicated to Professor H.-J. Cantow on the occasion of his 60. birthday**

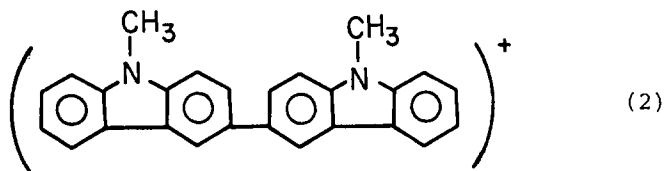
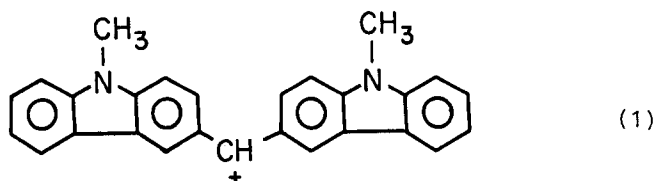
### Summary

N-methyl carbazole was reacted with dichloromethane or dibromomethane in the presence of  $AlCl_3$ ,  $SbCl_5$  or  $SnCl_4$  to give a polymer. In several cases insoluble structures with semiconductive properties were obtained. With dichloromethane and  $AlCl_3$ , a linear polymer: poly(N-methyl-3,6-carbazolyl methylene) (PMCM) was obtained. Charge transfer complexes of PMCM with acetyl-2'-hydroxyethyl-3,5-dinitrobenzoate generate a signal in the ESR spectrum, whose intensity does not depend on illumination. Films of complexes of PMCM are photoconductive with a maximum photocurrent in the visible region.

### Introduction

Polymers containing 3-substituted carbazole and 3,5-dinitrobenzoic acid derivatives as complexing groups have photoconductive properties (NATANSOHN and FLAISHER, in press, in preparation). Their near-infrared photoconductivity was assigned to an ion-pair formation through a proton transfer from carbazole to the nitro group. The photoconductivity is paralleled by an ESR signal increase with light (NATANSOHN, in press).

There are two possible structures of the carbazole cations:



Both were probable for polymers obtained from N-methyl-3-hydroxymethyl carbazolyl acrylate, and both could be responsible for the photosensitivity (NATANSOHN, in press) and photoconductivity (NATANSOHN and FLAISHER, in press).

In order to elucidate which of the structures (1) and (2) is generating the near-infrared photocurrent we proceeded to synthesize another polymer that can generate only one cation structure: (1).

Synthesis of poly(N-methyl-3,6-dicarbazolyyl methylene) (PMCM) was previously reported by polycondensation of N-methyl carbazole with formaldehyde (WATARAI, 1979). No molecular weight or glass transition data were reported. Also, there is a rather high quantity of gel formation (34%). A similar reaction was performed on poly(N-vinyl carbazole) generating a crosslinked polymer (BISWAS et al., 1984).

This paper presents the synthesis of PMCM by Friedel-Crafts polycondensation of N-methyl carbazole with dichloromethane and dibromoethane, using  $AlCl_3$ ,  $SbCl_5$  and  $SnCl_4$  as catalysts. The procedure is somewhat similar to that used by RAO et al. (1983) for the polycondensation of dibenzofuran with dichloromethane. The choice of this method was prompted also by a paper of PARTRIDGE (1983), which discussed different carbazole cations in dichloromethane in the presence of  $SbCl_5$ .

### Experimental

N-methyl carbazole was synthesized and purified as described previously (NATANSOHN, in press). Dichloromethane, dibromomethane, aluminium chloride (Merck), antimony chloride (Kodak) and stannic chloride (Fisher) were used as received. Acetyl-2'-hydroxyethyl-3,5-dinitrobenzoate (DNBAC, SIMIONESCU et al., 1982) and poly(acryloyl-2'-hydroxyethyl-3,5-dinitrobenzoate) (PDNBA, NATANSOHN, 1984) were synthesized as described in literature.

In a typical polycondensation procedure, the catalyst and the solvent were heated together at reflux (dichloromethane) or at 60°C (dibromomethane) until a homogenous mixture was obtained. Then, N-methyl carbazole was added in one portion and the reaction was kept at the same temperature for ca. 6 hours. A sharp change in color was observed when N-methyl carbazole was added, but the color was not always stable during the reaction. The procedure described by Rao et al. (1983) did not give any polymer.

During the reaction a precipitate was obtained in several cases. This was separated from the solution, washed and dried. The solution was chromatographed on alumina columns, concentrated and then precipitated with methanol. When no precipitate was obtained the solvent was evaporated and the solid product analysed. When a precipitate was obtained it was filtered, dried and reprecipitated for purification. A summary of the experiments is given in Table 1.

FTIR spectra were obtained on a Nicolet MX-1 spectrometer. Proton-NMR spectra were obtained on a varian CFT-20 spectrometer. Glass transitions were measured on a Mettler TA-3000 system. ESR spectra were taken on a Varian E-12 spectrometer. Molecular weights were measured by GPC on a column calibrated according to the polystyrene universal standard and were also calculated from the end groups in the NMR spectrum.

Electrical conductivity measurements were performed pellets with a two-probe automatic capacitance bridge assembly. Photoconductivity measurements were done by the time-of-flight method on spin coated samples on conductive quartz. The procedure of obtaining the spectral response is described in detail elsewhere (NATANSOHN and Flaisher, in press).

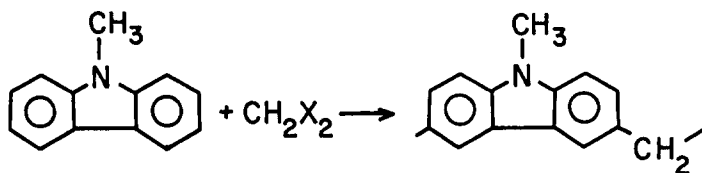
### Results and discussion

The expected scheme of polycondensation is:

Table 1  
Polycondensation experiments

No.	CH <sub>2</sub> X <sub>2</sub> X=	Catalyst	Catalyst quantity (mole)	Color during reaction	Results	
					Insoluble fraction	soluble in CH <sub>2</sub> X <sub>2</sub> , ins. fraction in CH <sub>3</sub> OH
1	Cl	AlCl <sub>3</sub>	0.011	green+brown	-	+(a)
2	Cl	AlCl <sub>3</sub>	0.00055	violet+green	-	+(a)
3	Cl	SbCl <sub>5</sub>	0.011	green	+	+(b)
4	Cl	SbCl <sub>5</sub>	0.00055	green	+	+(b)
5	Cl	SnCl <sub>4</sub>	0.011	violet+green	-	+(a)
6	Br	AlCl <sub>3</sub>	0.011	green	+	+(a)
7	Br	SnCl <sub>5</sub>	0.00055	green	+(*)	+(b)
8	Br	SnCl <sub>5</sub>	0.011	green	+(*)	+(b)

In all the experiments 20 ml CH<sub>2</sub>X<sub>2</sub> and 1 g (0.0055 mole) N-methyl carbazole were used.  
 (\*) Small quantity. (a) The NMR spectrum indicates an unsubstituted carbazole.  
 (b) The NMR spectrum indicates a monosubstituted carbazole.



Scheme 1

However, as it can be seen in Table 1, a multitude of soluble and insoluble structures are formed, depending on the nature of reactant and catalyst and on the catalyst quantity.

Several conclusions can be drawn from Table 1:

- Of the catalysts used  $\text{SbCl}_5$  seems the most active. It gives insoluble structures, and the soluble residue has a NMR spectrum characteristic to a monosubstituted carbazole, i.e. monohaloalkylated in position 3 or dimer.
- Aluminium chloride is less active, generating no insoluble structures in the reaction with  $\text{CH}_2\text{Cl}_2$ , and soluble reaction product has a NMR spectrum characteristic to unreacted carbazole. Catalytic amounts of  $\text{AlCl}_3$  seem almost inactive, whereas molar amounts (one mole for one reaction site) generate an insoluble fraction (Exp. 6) or a linear polymer (the fraction soluble in  $\text{CH}_2\text{Cl}_2$  and insoluble in  $\text{CH}_3\text{OH}$  in Exp. 1).
- Stannic chloride is practically inactive.

In similar conditions, RAO et al. (1983) obtained from dibenzofuran and dichloromethane, with  $\text{AlCl}_3$  as catalyst, an insoluble colored polymer, and they explained the color and insolubility by crosslinking and ring fusion. Our attention has been directed towards the linear soluble polymer which constitutes a macromolecular model for structure (1). This is obtained in Exp. 1 (Table 1) as the fraction soluble in  $\text{CH}_2\text{Cl}_2$  and precipitated with methanol. From the proton NMR spectrum (Figure 1) the structure is consistent with that presented in Scheme 1: at 7.90 ppm the 1 and 8 aromatic protons of carbazole, at 7.23 ppm the 2,4,5 and 7 aromatic protons. The absence of ortho-coupling in the signal at 7.90 ppm indicates the substitution in positions 3 and 6. The signal at 4.31 ppm is the methylene bridge, and the signal at 3.78 ppm is the methyl group. The methylene end groups give a signal at 4.72 ppm, which permits to calculate the average molecular weight.

The results correlate very well with the GPC results, and indicate that the molecular weight increases slowly during the reaction. At ca. 6 hours a  $\overline{\text{DPn}}$  of 3.5 is obtained, whereas at 48 hours  $\overline{\text{DPn}}$  increases to ca. 5.

Further confirmation of the linear structure is given by the FTIR spectrum - Figure 2.

The two intense absorptions at 745 and 721  $\text{cm}^{-1}$  characteristic for an unsubstituted carbazole (ortho-disubstituted benzene ring) are not present. Instead, at 797  $\text{cm}^{-1}$  the out-of-phase aromatic CH vibration characteristic to the 1,2,4 substitution in the benzene ring (corresponding to a 3,6-substitution in carbazole) is very intense.

One can therefore conclude that the middle fraction of Exp. 1 (Table 1) is linear PMCM. The polymer is brown-colored and we cannot find any explanation for the color. The glass transition temperature of the polymer is 170° C.

The insoluble fractions obtained in Exp. 3,4,6,7 and 8 are insoluble in any organic solvents, have a metallic shine and a dark green color. Their FTIR spectra indicate that the catalyst used in the reaction is still present as an electron acceptor complexant. If their structure is similar

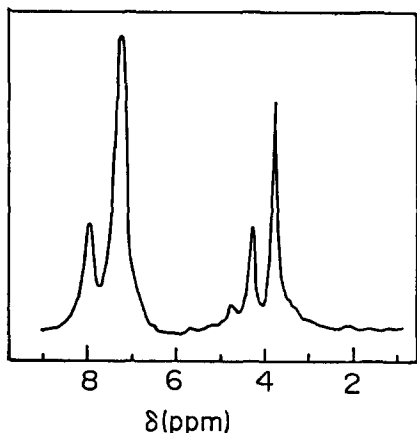


Fig.1  $^1\text{H}$  NMR spectrum of PMCM in  $\text{CDCl}_3$

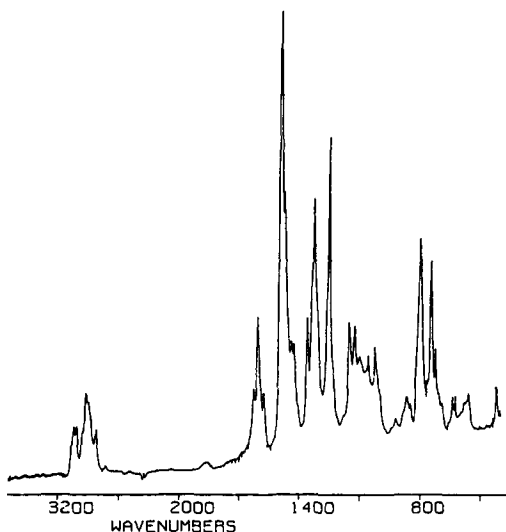


Fig.2 FTIR spectrum of PMCM (KBr pellet)

to that postulated by RAO et al. (1983), i.e. containing fused rings, then they should present some electrical conductivity. Recently, WELLINGHOFF et al. (1983) and JENEKHE et al. (1984) demonstrated a very high electrical conductivity for poly(3,6-carbazolyl) doped with iodine. The results of the electrical conductivity measurements performed on our samples are presented in Table 2.

Table 2  
Electrical conductivity

Sample	Electrical conductivity ( $\text{ohm}^{-1} \text{cm}^{-1}$ )
Linear PMCM	$2 \times 10^{-10}$
Linear PMCM doped with $\text{I}_2$	$8 \times 10^{-6}$
Insoluble fraction, Exp. 3	$1 \times 10^{-6}$
Insoluble fraction, Exp. 4	$2 \times 10^{-6}$
Insoluble fraction, Exp. 6	$2 \times 10^{-5}$

Indeed, the insoluble structures are semiconductive, with an electrical conductivity slightly higher than that of iodine-doped PMCM. The pure PMCM is an insulator.

Photosensitivity studies were made on a sample of PMCM mixed with DNBAc in chloroform solution. The ESR spectrum is presented in Figure 3. The spectrum is very similar to that obtained for poly(N-methyl-3-hydroxy-methyl carbazolyl acrylate - co - acryloyl-3'-hydroxypropyl-3,5-dinitrobenzoate) (p(MCMA-co-DNBPA)), except that no hyperfine structure is

obtained. This is probably due to the presence of carbazole in the main chain, which considerably reduces the mobility. But, whereas for p(MCMA-co-DNBPA) a 4.4-fold increase was obtained in chloroform in the presence of light, the ESR signal of PMCM + DNBAC is not sensitive to light.

The spectral responses of PMCM (a), a 2:1 mixture of PMCM and DNBAC (b) and a 1:1 mixture of PMCM with PDNBA (c) are presented in Figure 4. As expected, PMCM presents a weak photocurrent as compared with the charge transfer complex PMCM-DNBAC. No near-infrared photocurrent is generated by PMCM. Surprisingly, the most intense photoresponse is given by the mixture of the two polymers: PMCM and PDNBA. This mixture has also a slightly increased near-infrared photocurrent. However, when comparing with p(MCMA-co-DNBPA) (NATANSOHN and FLAISHER, in press), the near-infrared photoresponse is not significant.

Consequently, according to the evidence presented here, one can conclude that structure (1) is not the one responsible for photosensitivity and photoconductivity.

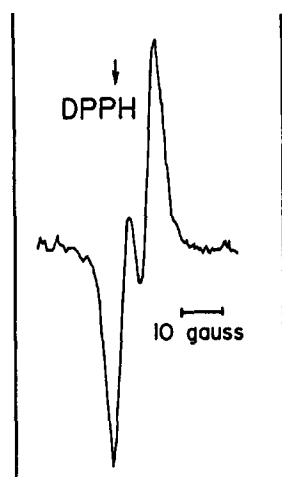


Fig.3 ESR signal of PMCM+ DNBAC in chloroform

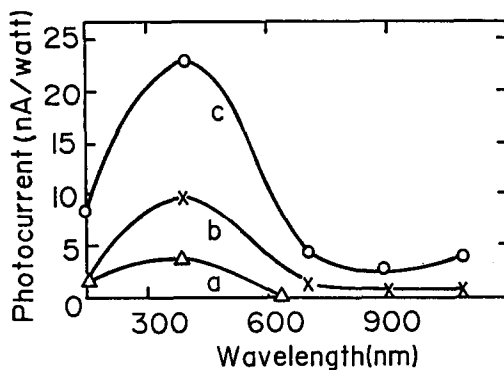


Fig.4 Spectral response of PMCM (a), PMCM+ DNBAC (b) and PMCM+PDNBA (c). The photocurrent is normalized with respect to incident light. Voltage bias =0.8 mV.

#### References

- BISWAS, M., BAGCHI, S. and URYU T., *J. Appl. Polym. Sci.*, 29, 1183 (1984)  
 JENEKHE, S. A., WELLINGHOFF, S. T. and REED, J. F., *Mol. Cryst. Liq. Cryst.*, 105, 175 (1984)  
 NATANSOHN, A., *Polymer Preprints*, 25 (2), XXX (1984)  
 NATANSOHN, A., *J. Polym. Sci., Polym. Chem. Ed.*, in press  
 NATANSOHN, A. and FLAISHER, H., *J. Polym. Sci., Polym. Lett. Ed.*, in press  
 NATANSOHN, A. and FLAISHER, H., in preparation  
 PARTRIDGE, R. H., *Polymer* 24, 733 (1983)  
 RAO, S. P., JONES, M. B., BÄLTISBERGER, R. J., BURGER V. T. and BROWN, C. E., *J. Polym. Sci., Polym. Lett. Ed.*, 21, 551 (1983)  
 SIMIONESCU, C. I., PERCEC, V. and NATANSOHN, A., *J. Polym. Sci., Polym. Chem. Ed.*, 20, 63 (1982)  
 WATARAI, S., *J. Polym. Sci., Polym. Lett. Ed.*, 17, 655 (1979)  
 WELLINGHOFF, S. T., KEDROWSKI, T., JENEKHE, S. and ISHIDA, H., *J. de Physique, Coll. C3*, 44, 677 (1983)