

# Catalytic Dehalogenation Polymerization of 4,4'-Dihalogenetriphenylamines in the Presence of a Nickel Complex

*Olga K. Kocheleva, Sergey A. Lebedev, Boris V. Kotov, Eduard. S. Petrov, Alek R. Tameev\*, Alexey A. Kozlov\*, and Anatoly V. Vannikov\**

*Karpov Institute of Physical Chemistry, 10, Voronzovo Pole, Moscow 103064 Russia;*

*\* A.N. Frumkin Institute of Electrochemistry of the Russian Academy of Sciences Leninskii Pr., 31, Moscow 117071 Russia*

## Abstract

Triphenylamine oligomers (OTPA, n=4-10) were synthesized by dehalogenation polymerization of 4,4'-dihalogenetriphenylamines. The OTPAs are a white powder, which is stable on exposure to the air and soluble in benzene, chlorobenzene, chloroform and THF. The OTPAs were characterized by IR, H-NMR and UV-visible spectroscopy measurements. OTPA films prepared by casting from solutions or vapor deposition exhibit a high drift mobility of holes and accordingly double layer organic photoconductors including the OTPA layer show a high electrophotographic sensitivity.

## Introduction

While the recent advancement of performance of organic photoreceptors has made them applicable to high-speed copying machines and printers, the-state-of-art organic photoreceptors are not necessarily sufficient in terms of performance when applied to high-speed copying machines and printers. In particular, improvement in durability of organic photoreceptors has been demanded. Although molecularly doped polymer systems, which are widely used as charge transporting layers (CTLs) exhibit satisfactory electrical characteristics, they inherently have a poor abrasion resistance because the addition of the charge transporting molecules to the binder polymer causes a deterioration of a mechanical strength of the binder, and therefore, the CTL is fragile and has a low tensile strength. It is considered that the above-mentioned deterioration of the mechanical strength of the binder polymer causes CTL disadvantages such as wears, flaws, peelings, and cracks. Further, when applied to electroluminescence devices, a low-weight molecular CTL tends to melt due to generated Joule's heat and to crystallize, which cause morphologic changes of the film. This paper describes the synthesis of oligomeric triphenylamines, its xerographic properties with expectation of eliminating the above-mentioned disadvantages.

## Experimental

### Materials

4, 4'-dichlorotriphenylamine was prepared as following manner. 4,4'-diaminotriphenylamine was diazotated in hydrochloric acid (aq.) at +2° C in an argon atmosphere (Fig. 1). Then the reaction mixture was added to the solution of CuCl in hydrochloric acid under stirring. That was Sandmeyer reaction<sup>1</sup> (Fig. 2), which had a radical mechanism via halogen-complexed organo-cuprate intermediate<sup>2</sup>. The organic residue was recovered by filtration and washed tho-roughly with water. The monomer was dissolved into benzene and heated while stirring. Any insoluble matter was removed by filtration, and the filtrate was poured into hexane under stirring. The resulting filtrate was evaporated and the red oil was chromatographed on silica gel with hexane elution and recrystallized from acetic acid to give a white crystalline powder. Yield: 44.2%. Mp°C.. 83° C. Anal. Calc. for C<sub>18</sub>H<sub>13</sub>NCl<sub>2</sub>: C, 68.79; H, 4.14; N, 4.46; Cl, 22.61. Found: C, 68.72 ; H, 4.43; N,4.47; Cl, 22.38. The same monomer obtained through an Ullmann reaction between aniline and 4-chloriodobenzene with copper powder and potassium carbonate<sup>3</sup> had Mp. 83-84.5°C.

4, 4'-Dibromotriphenylamine was obtained in the same manner as 4, 4'- dichlorotriphenylamine except that hydrochloric acid was changed on hydrobromic acid and 4, 4'-dibromotriphenylamine was the light oil. Yield: 47.5%.

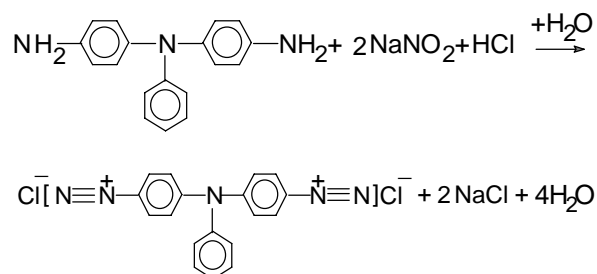


Figure 1. The diazotation of 4,4'-diaminotriphenylamine in hydrochloric acid (aq.)

Bis-(triphenylphosphine) nickel dichloride was prepared according to the literature method<sup>4</sup>. Other chemicals were commercially obtained.

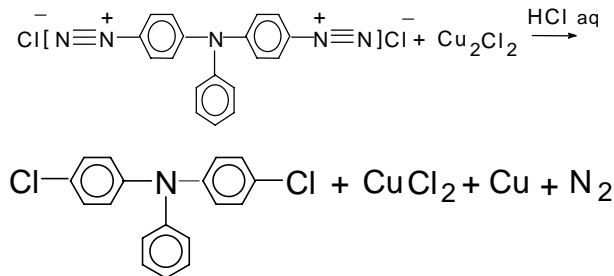


Figure 2. The preparation of 4, 4'-dichlorotriphenylamine by Sandmeyer reaction<sup>1</sup>

### Polymerization

Oligomeric triphenylamines were synthesized by nickel-promoted dehalogenation polymerization of 4, 4'-dihalogenotriphenylamines (Fig. 3). A mixture of 2 g (6.4 mmol) of monomer, 0.65 g (2.5 mmol) of triphenylphosphine, 0.84 g (1.28 mmol) of bis-(triphenylphosphine) nickel dichloride, 1.58 g (24.2 mmol) of zinc dust and 30 ml of de-aerated dry N-methyl-2-pyrrolidone (NMP) was stirred at 55° C for about 3 (OTPA-1), 8 (OTPA-2), 24 (OTPA-3) hrs under an argon atmosphere. After the polymerization the reaction mixture was filtrated and poured into 1 l of 10% hydrochloric acid (aq.). The precipitated pale yellow oligomers were washed with water and acetone and separated by filtration. Then the dried oligomers were dissolved in chloroform and reprecipitated in diethyl ether and hexane for six times. The resulting oligomers were obtained as white powders, were soluble in chlorobenzene, benzene, chloroform, NMP and were stable in air. Yield for oligomeric TPA from 4, 4'-dibromotriphenylamine and 4, 4'-dichlorotriphenylamine was from 75% to 85%.

The oligomeric PTPA-3 give log  $\mu$  value of 0.08 dL g<sup>-1</sup> in NMP at 25° C and show Mn and Mw values of 1250 and 2300, respectively, as determined by GPC (eluent = THF; vs. polystyrene). At shorter polymerization time, e.g. 3 and 8 hrs, the oligomers show lower Mw values of 1154 and 1680, respectively.

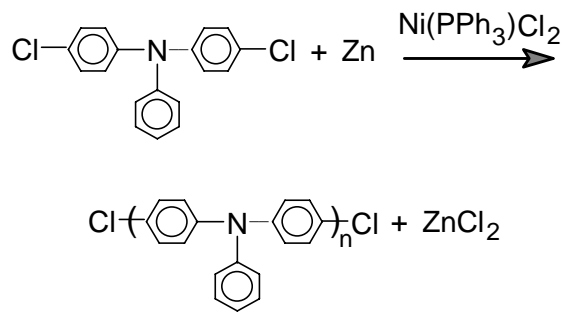


Figure 3. The preparation of oligomeric TPA

### Preparation of OPC using DEH, TPD and Oligomeric TPA as Hole Transport Material (HTM)

A dual layer type OPC film (Figure 4) which was comprised of oligomeric TPA as HTM consisted of an polyethyleneterephthalate substrate with In<sub>2</sub>O<sub>3</sub>:SnO<sub>2</sub> (9:1) electroconductive layer, a barrier-adhesion layer (BAL) of 0.8-1.2 microns thick, a generation layer of 0.5-0.8 microns thick, and a transport layer of 8-12 microns thick. Barrier-adhesion layer was cast from a solution of a milk casein or polyamide (PA 6/66/610). Charge generation layer was composed of metallic phthalocyanine (TiOPc) pigment dispersed in polyvinylethylal (2:1). Charge transport layers (CTL) were either 4-(diethylamino)benzaldehyde diphenylhydrazone (DEH), N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) and oligomeric TPA dispersed PC or TPD and oligomeric TPA without polymer binder. The layers were prepared by the doctor blade, the dip coating methods and by vapor deposition. TiOPc has been produced from phthalonitrile and TiCl<sub>4</sub>. The product was then washed with water and with organic solvents, treated with acid paste and finally again washed with water and organic solvents. Further it was crushed by vibration and ultrasonic mill. DEH has been synthesized through the equimolar reaction of 1,1'-diphenylhydrazine and 4-(diethylamino) benzaldehyde. Then the crude hydrazone was recrystallized with ethanol or n-hexane. TPD (ST 16/1.2, SynTec GmbH) was used without purification. PC-3 (PO " Zarya", Russia) with molecular weight equal to ca 30000 and with melting index (168° C/1.2 kg) equal to ca 7.1-7.6 g/10 min< was used as polymer binder (PB) for CTL.

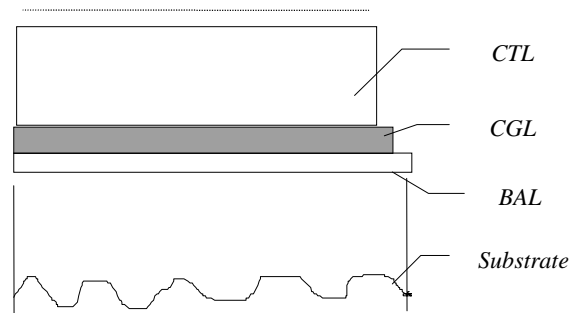


Figure 4. Schematic diagram of dual layer OPC

Sensitivity  $S_1$  (lx·s)<sup>-1</sup> was determined by reciprocal exposure required to reduce the corona charged surface potential to halfvalue. Charge carrier mobility in CTL was measured by conventional time-of-light (TOF) techniques<sup>5</sup>. For these measurements, sandwich type samples were prepared by casting of corresponding solution onto a polished stainless steel substrate and dried at 80-90° C. The thicknesses of CTLs were 4.6-6.6 microns. A generation layer (selenium or titanium oxide phthalocyanine) of 0.2-0.3 microns thick was deposited on CTL free surface and finally an upper aluminium semitransparent electrode was deposited on it. Both the generation layer and the upper electrode were deposited by thermal evaporation in vacuum of 10<sup>-6</sup>-10<sup>-5</sup> Torr. A 337.3 nm N<sub>2</sub> laser pulse of 10 ns

duration absorbed by the generation layer was used for the photogeneration of the free charge carriers. Transient currents were recorded by a digital oscilloscope Tektronix TDS340A. Measurements were carried out at small signal mode of TOF:  $q < 0.1$  CV, where  $q$  is an injected charge,  $C$  is the sample capacitance,  $V$  is the applied voltage. The relative permittivity of polymeric films was calculated from data of high-frequency conduction measurements made with an accuracy of 10%. The thickness of films was measured with microinterferometers MII-4 or MII-40. Both xerographic and TOF measurements were carried out at room temperature.

Figure 5 shows IR spectra of oligomeric TPA (a) and 4,4'-dichlorotriphenylamine (b). The IR spectrum of 4,4'-dichlorotriphenylamine showed 5 bands at 1290 (1310), 1480, 1580, 820 and 710  $\text{cm}^{-1}$ , assignable to the C-N stretching vibration of tertiary amines, the C-C skeleton vibration and the C-C stretching vibrations, the C-H deformation of 1,4-disubstituted benzene rings and the C-Cl stretching vibration, respectively. The IR spectrum of oligomeric TPA contains the same absorption bands attributed to the triphenylamine structure, but the band at 710  $\text{cm}^{-1}$  was too weak, due to the C-Cl stretching vibration of the terminal benzene rings. These results indicate that a C-C bond was formed between the monomers at the carbon atoms coupled with chlorine originally and a highly conjugated system was formed.

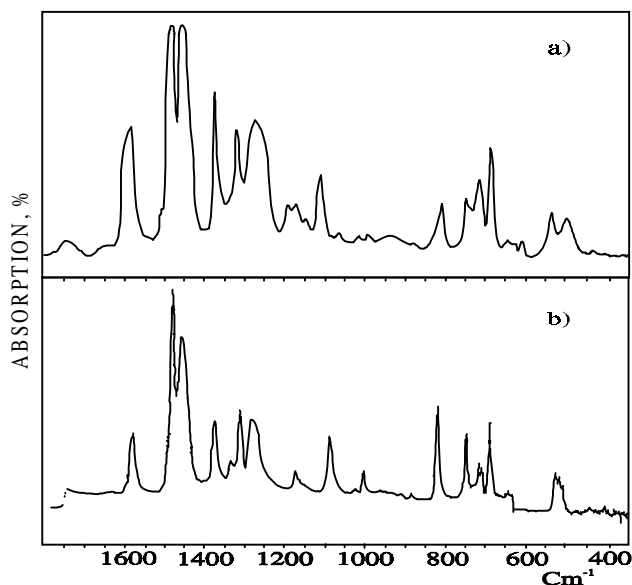


Figure 5. IR-spectra of oligomeric PTPA (a) and 4,4'-dichlorotriphenylamine (b).

The  $^{13}\text{C}$  NMR spectrum of oligomeric TPA shows four bands at 124.1, 127.2, 129.2 and 134.6 ppm., which were assignable to biphenylene carbon resonances, due to the polymerization of 4,4'-dichlorotriphenylamine.

#### Electrophotographic Properties of OPC

In Table 1, the xerographic properties of OTPA, DEH and TPD doped PC are listed. As Table 1 shows,

electrophotographic characteristics of oligomeric TPA improve with increasing their molecular weights. Thus, the photosensitivity of PTPA-3 is almost comparable to those of DEH and TPD.

Figure 6 shows the hole drift mobility as a function of electric field strength for OTPA doped polycarbonate PC-3 and OTPA without polymer binder. As follows from Figure 6., the mobility of OTPA doped PC-3 (1:1) was less than ones for TPA<sup>6</sup>, DEH<sup>7</sup> and TPD<sup>8</sup>, while the mobility of pure PTPA ( $\mu = 2 \times 10^{-5} \text{ cm}^2 / (\text{V}\times\text{s})$ ,  $F^{1/2} = 800 \text{ (V/cm)}^{1/2}$ ) was one or two orders of magnitude higher than these data. The increase in the hole drift mobility for pure PTPA can be attributed to the fact that a favourable conformation of polymer chains to charge carrier transport was formed in the self-ordered polymer photoconductor.

**Table 1. The electrophotographic sensitivity of photoreceptors with different OPC. CTL is OPC+PC-3 (1:1), CGL is TiOPc + PVB (2:1).**

Photo-receptor, No	OPC	$M_w$	Photosensitivity, S, $(\text{l}\times\text{s})^{-1}$
1	PTPA-1	1154	2.9
2	PTPA-2	1680	2.9
3	PTPA-3	2300	3.5
4	DEH		3.3
5	TPD		2.9

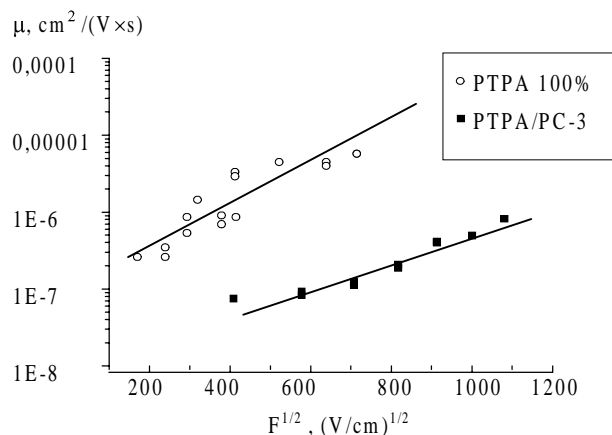


Figure 6. Field dependence of hole drift mobilities for polycarbonate PC-3 doped by PTPA and pure PTPA. The doped OPC concentration was 50 wt. % and the temperature was 295 K.

It was suggested that the role of the polymer binder was related to the increasing of distance between the dopant aggregates in the host and to reducing of compatibility of components in the charge transport layer.

Moreover, semiempirical calculations of charge distribution on neutral molecule and cation-radical of OTPA ( $n=4$ ) were performed by a PM3 method. The calculation shows that the highest occupied molecular

orbital (HOMO) distribution on the neutral molecule of OTPA was the same as for separate TPA molecule. While for cation-radical the positive charge is localized on the nitrogen atom of a side triphenylamine unit. So possible only a part (20-50%) of OTPA amines provides the charge transport through a medium. Therefore, the hole mobility in the binderless OTPA films is lower when compared with binderless TPD films<sup>9-11</sup>. But the electrical properties of vapour-deposited TPD film are not stable and reproducible<sup>11</sup> and otherwise that of OTPA film are stable.

### Conclusion

We have synthesized oligomeric triphenylamines (OTPA) using a novel method of dehalogenation polymerization of 4,4'-dihalogenetriphenylamines in the presence of a nickel catalyst and zinc dust. These compounds doped polycarbonate showed xerographic properties which were comparable to those for DEH and TPD. The hole drift mobility of pure PTPA was higher than ones for DEH, TPD and PTPA doped polycarbonate. These results indicated that oligomeric TPA can be useful for a negative charging electrophotographic materials.

### Acknowledgments

The research carried out at Frumkin Institute of Electrochemistry was made possible by the International Science and Technology Center grant 872, and the Russian Fond for Basic Research grant 96-03-34315.

### References

1. H. Sandmeyer, Ber., 17, 1633, (1884).
2. E. Pfeil, O. Velten, Ann., 562, 163, (1949).
3. M. Ishikawa, M. Kawai, Y. Ohsawa, Synthetic Metals, 40, 231-238, (1991).
4. L. M. Venanzi, J. Chem. Soc., 719, (1958).
5. P. M. Borsenberger, D. S. Weiss, Organic Photoreceptors for Imaging Systems, Marsel Dekker, New York, (1993).
6. G. Pfister, Phys. Rev. B., 16, 3676, (1977).
7. T. Kitamura, M. Yokoyama, J. Appl. Phys., 69, 821, (1991).
8. H.-J. Yuh, D. M. Pai, Mol. Cryst. Liq. Cryst., 183, 217, (1990).
9. M. Stolka, J. F. Yanus, and D. M. Pai, J. Phys. Chem., 88, 4707, (1984).
10. Abkowitz and D. M. Pai, Phil. Mag., B. 53, 193, (1986).
11. T. Mori, E. Sugimura, and T. Mizutani, J. Phys. D: Appl. Phys., 26, 452, (1993).

### Biography

Olga K. Kocheleva graduated from the St.-Petersburg Institute of Cinema and Television (St.-Petersburg, Russia) in 1993 on the speciality of technology of photographic materials. 1993 - 1996 - researcher at the "Scientific Research Phototechnical Institute on Company Slavich ("NIFTI-Slavich", Pereslavl- Zalessky). 1993 - 1997 - postgraduate student at the Karpov Institute of Physical Chemistry. Since 1997- researcher at this Institute. ca. 5 publications.

E-mail: nifti@nifti.users.botik.ru or: kochel@cc.nifhi.ac.ru