An Influence of Polycarbonate Molecular Weight and Structure on Hole Drift Mobility and Electrophotographic Properties of Photoconductors

Olga K. Kocheleva, Konstantin K. Kochelev
NIFTI-Slavich (Scientific Research Phototechnical Institute on Slavich Co.)
Pereslavl-Zalessky, 152140, RUSSIA

Alek R Tameev, Alexey A. Kozlov and Anatoly V. Vannikov
A.N. Frumkin Institute of Elecrtochemistry of RAS
Leninsky Pr.,31, Moscow, 117071, RUSSIA

Abstract

Hole transport and electrophotographic properties of organic photoconductors (OPC) on the base of 4-(di-ethylamino)benzaldehyde-N,N'-diphenylhydrazone (DEH) and phenyl-4-tolyl-2-naphtylamine (PTNA) doped polymer binders such, as bisphenol-A-polycarbonates (PC-A), bisphenol-Z-polycarbonates (PC-Z) with different molecular weights, polymethyl methacrylate (PMMA) and others was investigated. Hole drift mobility was measured by the conventional time-of-flight (TOF) techniques and discussed in terms of Gill approach, disordered model and correlated dipole model. Influence of structure and molecular weight of polymer binder and concentration of OPC on the hole mobility and electrophotographic properties have been investigated.

Introduction

Our previous paper[1] reported on the hole transport and electrophotographic properties of DEH doped PC-A with different molecular weight (PC-1 and PC-3). The molecular weight of PC-1 was approximately two times higher than that for PC-3.

It was shown[1], that the concentration dependencies of the xerographic sensitivity S_L for DEH doped polycarbonates PC-3 and PC-1 in the range of 10 - 50 wt. % are similar, and their values of the sensitivity are closely spaced. However, at DEH concentration of 5 wt. % the DEH+PC-1 system has no sensitivity unlike the DEH+PC-3 system. The possible explanation for this fact is a various structural order of molecules DEH in PC-1 and PC-3 polymer matrices that is especially displayed at low concentration of DEH. Furthermore, the hole drift mobility for fragile and inflexible PC-3 films was larger than for flexible PC-1 films. It was linked with different mobility of segments and lateral groups of polymers in charge transport layer (CTL) or with different structure of the films.

At this work we have continued the study of an effect of polymer characteristics (in particular, structure and molecular weight) on hole transport and electriphotigraphic properties of OPC (PTNA, DEH) doped PC-A, PC-Z, polymethyl methacrylate (PMMA) and some other polymers.

Experimental

The samples studied by xerographic method consisted of an polyethylenterephthalate substrate with $In_2O_3xSnO_2$ (9:1) electroconductive layer, a barrier-adhesion layer 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 polyamide (PA 6/66/610). Charge generation layer was composed of vanadyl or titanil phthalocyanine (PcVO, TiOPc) dye dispersed in polyvinylethylale (2:1). Charge transport layers were DEH or PTNA dispersed PC-A: PC-1 and PC-3 (PO "Zarya", Russia), PCA (Australia); PC-Z: PC-ZE (E-2000, Mitsubishi Chemical Co.), Iupilon Z-200, Z-300 and Z-400 (Mitsubishi Gas Chemical Co.); PMMA (LSO-M, $M_w \cong 100\,000$, PO "Orgsteclo"); polyvinyl naphthalene (PVN); polysulfone-A (PSN, Union Carbide); poly-α-methyl styrene (PMS).

The specific viscosity of 0.5 g/dl solutions of the polymers was measured in dichloromethane (20^0 C). PC-1 and PC-3 have melting indexes (168 ^{o}C /1,2 kg) equal to ca 3.0 - 3.5g/10 min and 7.1 - 7.6g/10 min, respectively. PC Z-200, PC Z-300 and PC Z-400 have molecular weights equal to 20000, 30000 and 40000, respectively.

The layers were prepared by the doctor blade and the dip coating method.

Sensitivity for Halogen Lamp (T_{color} = 2850 K) $S_{1/2}$ $(lx\times s)^{-1}$ was determined by measuring the exposure required to reduce the corona charged surface potential to halfvalue.

Hole drift mobility in charge transport layer (CTL) was measured by conventional time-of-flight (TOF) techniques that have recently been reviewed [3]. Sandwich type samples were prepared for these measurements. In this case corresponding solutions were cast onto the polished stainless steel substrate or glass substrate with the indium-tin-oxide (ITO) electroconductive layer and dried at 80 - 90° C. Thickness of the CTLs ranged between 4 and 7μm as determined by a microinterferometer MII-4 and calculated from a CTL's capacitance. A 0.2-0.3 μm thick generation layer of selenium or titanium oxide phthalocyanine was deposited on the CTL free surface. Finally, a top aluminium semitransparent electrode was deposited on the generation layer. Both the generation layer and the top electrode were deposited by thermal evaporation in vacuum of 10^{-5} Torr. The TOF measurements were made at room temperature. A 337.3 nm N_2 laser pulse of 10 ns duration absorbed by the generation layer was used for the photogeneration of the free charge carriers. Measurements were carried out at a small signal mode of the TOF method; that is, the maximum charge generated at the electrode surface was less than 0.05 CV, where C is the sample capacitance and V the applied voltage. The transient currents were measured with a digital oscilloscope Tektronix TDS 340A providing that $R_L C_C << t_T$ was always fulfilled, where R_L is the load resistor, C_C is the capacitance of circuit and t_T is a transit time. The transit time was determined from the intersection of the asymptotes to the plateau and the tail of the transient. This time corresponds to the moment of the carriers sheet front arrival to an opposite electrode. The drift mobility was determined from the conventional expression $\mu=d/(F\ t_T)$, where F is the applied field and d is the CTL thickness. Mobility values were obtained with an accuracy of 15%. Both xerographic and TOF measurements were carried out at room temperature.

Hardness of layers was measured by determination of depth of diamond pyramid (dimensions of imprinted diagonals of pyramid) pressed in films at fixed times and pressure.

Results and Discussion

Figs. 1-4 show the hole mobility as a function of electric field strength for DEH and PTNA doped (1:1) polymer binders (PB) of different types. As follows from the Figs. the mobility strongly depends on the type of PBs and their molecular weights (MW). As the electric field increases the hole drift mobility raises accordingly.

The $F^{1/2}$ - lg μ plots yield practically straight lines in the range of $F^{1/2}$ > 300 - 400 $(V/cm)^{1/2}$, and at higher values of $F^{1/2}$ for DEH + PVN and PTNA + PC-ZE films.

Values μ for DEH + PC-3 (Fig.1) are larger than for DEH + PC-1 and other films. Values μ are practically equal for each DEH + PC-1, DEH + PC Z-200 and DEH + PC Z-400 films.

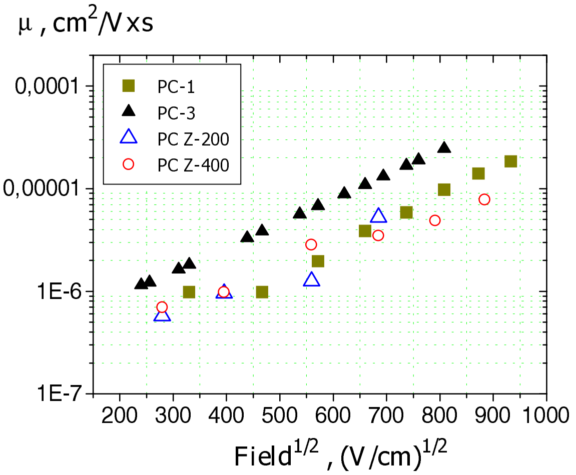

*Figure 1. Field dependence of hole drift mobility for DEH dispersed into polycarbonate with a different molecular mass. **30** - PC-3, **45** - PC-1, **200** - PC Z-200, **400** - PC z-400. The DEH concentration was 50 wt.%. T = 295 K.*

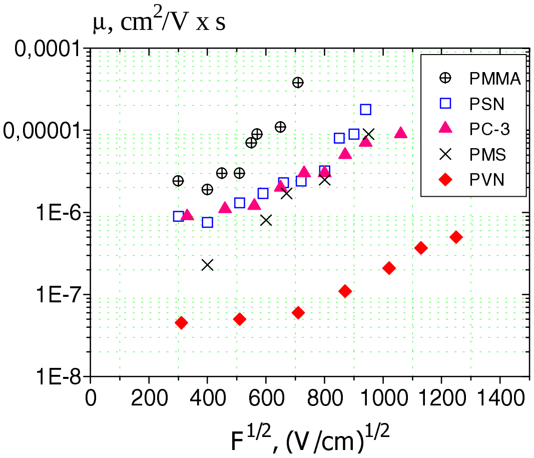

Figure 2. Logarithm of the hole drift mobility vs. $F^{1/2}$ for 50% DEH doped polymer binders. T= 295 K.

For DEH or PTNA doped PMMA films values of μ are the highest. Other films have lesser values of μ.

For DEH + PC-A systems the highest values of μ are peculiar to PC-3. DEH + PC-1, DEH + PC Z-200 and DEH + PC Z-400 films have lower values of μ, and they are practically equal.

Magnitudes of special viscosity η_S of polymers in identical conditions are shown in Table 1.

As is known, the higher special viscosity of polymer solution the higher molecular weight (MW) of polymer (for polymers with identical or similar nature). Therefore MW for PC-1 > PC-3 > PCA (for PC-A polymers) and MW for PC Z-400 > Z-300 > PC-ZE > Z-200 (for PC-Z polymers).

Thus, for DEH + PC-A films the lower MW the higher values of μ. But for PTNA + PC-A we can see an opposite tendency - the lower MW of polymer binder the lower μ. For DEH + PC-Z values of μ don't depend on MW.

For the PC+DEH system, mobility increases as electric field increases and the field dependence of mobility is linear in coordinates $lg\mu$ - $F^{1/2}$ over all the experimental range of electric field. As for the PC+PTNA system, mobility increases as electric field increases and the dependence is linear in the same coordinates at field higher than ~$5\cdot10^5$ V/cm only. To describe the charge carrier transport in disordered systems, a number of theoretical models have been developed. A Gaussian disordered formalism[3] and a correlated dipole model[4] (CDM) are of models of sufficient generality. The CDM is able to reproduce a wide experimental range of electric field and temperature and describe variation of *n* in the dependence $\mu \sim \exp(F^n)$.

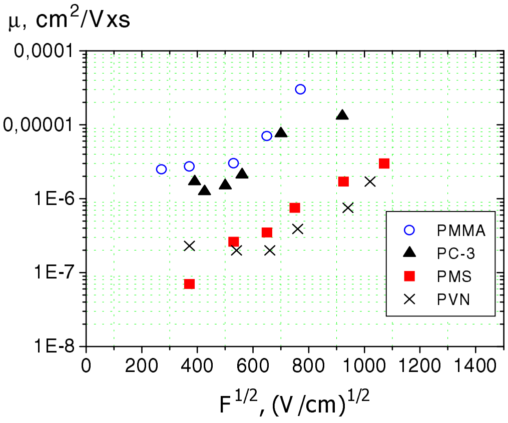

Figure 3. Logarithm of the hole drift mobility vs. $F^{1/2}$ for 50% PTNA doped polymer binders. T= 295 K.

Table 1. The specific viscosity of 0.5 g/dl solutions of polymer binders (η_s/C) in dichloromethane at 20 C^0.

Polymer binder	η_s/C *	Polymer binder	η_s/C *
PMMA	0,34	PC-3	0,78
PC Z-200	0,53	PC-1	0,96
PC- A (Australia)	0.62	Iupilon Z-300	0,99
PC- Z (E- 2000)	0.78	Iupilon Z-400	1,20

* $\eta_s = (t_1 - t_0)/ t_0$, where t_0 - time of solvent outflow, t_1 - time of solution outflow.

Thus, the obtained data (with the results of previous paper[1]) are evidence of significant influence of molecular weights of PBs on hole drift mobility for DEH and FTNA doped PC-A films.

In accordance with to earlier obtained data[1,2,5] one may conclude, that an influence of MW of PC-A and PC-Z on values $S_{1/2}$ is practically absent. Indeed, measured in this work values of $S_{1/2}$ for DEH + PC Z-200 (or Z-300 or Z-400), and for DEH (or FTNA) + PC-1 (or PC-3) are practically equal. Thus, defined visible correlation of values of μ (or $S_{1/2}$) and MW has not been observed.

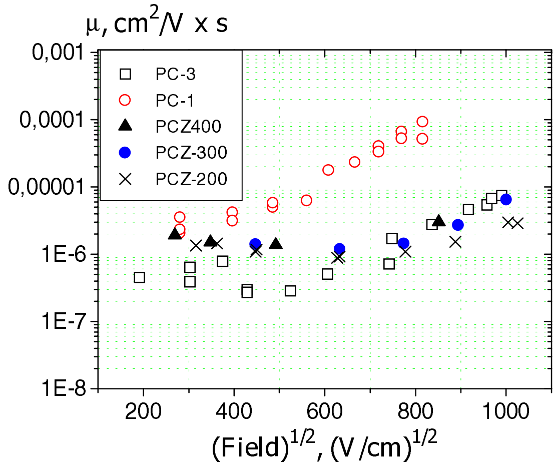

Figure 4. Field dependence of hole drift mobility for PTNA dispersed into polycarbonate with a different molecular mass. The PTNA concentration was 50 wt.%. .T = 295 K.

Seemingly, values of μ depend on some different factors- of a nature of OPC and polymer binder, of a technology of sample preparation (by means of a solvent composition, OPC concentration in solution, and the terms of drying of the covered layers) and so on.

The technology of sample preparation can also influence on technological compatibility of components of a layer, quantity and properties of OPC associates.

These factors can influence on different properties of layers, namely, on free volumes in CTL.

It was shown[6], that technology of sample preparation and accordingly values of free volumes can influence on hole drift mobility.

It is possible to suppose that presence of free volume in CTL can influence and on a microhardness of samples of PB and OPC+ PB films.

Accordingly, microhardness of PC-3 film is higher than the one of PC-1 film (≅ 15 %). Similarly relation for DEH doped (1:1) PC-1 or PC-3 is observed. At the same time microhardness of PC Z-200, Z-300 and Z-400 films (and also microhardness of DEH doped these PC-Z films) are practically equal.

Thus, the correlation between microhardness and hole drift mobility has been observed.

This can be indirectly evidence of an influence of free volume on electrophotographic characteristics of materials.

Thus, the research of influence of polymer binder on the characteristics of photoconductive layers requires comprehensive investigations of structure and properties of these layers and processes of film formation when casting from solutions.

Conclusion

Influence of structure and molecular weight of polymer binder and concentration of OPC on the hole mobility and electrophotographic properties have been found out. The correlation between microhardness and hole drift mobility has been observed. Structure and composition of photoconductive layers (and processes of film formation when casting from solutions) influences on characteristics of CTL and requires comprehensive investigations.

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Biography

Olga K. Kocheleva graduated from the St.-Petersburg Institute of Cinema and Television in 1993 (technology of photographic materials). 1993 - 1996 - researcher at the "Scientific Research Phototechnical Institute ("NIFTI-Slavich", Pereslavl- Zalessky). Since 1993 - postgraduate student, then researcher at the Karpov Institute of Physical Chemistry (Moscow). She studied polymeric chemistry (OPC) and electrophotographic materials. In 1999 she received her Dr. degree in technical sciences (OPC photoreceptors).
6 publications. **E-mail**: kosh@knifti.users.botik.ru or: kochel@cc.nifhi.ac.ru

Alek R.Tameev graduated from the Moscow Institute of Physics and Techniques (Department of Molecular and Chemical Physics) in 1981 with B.Sc.and did his postgraduate studies at the Frumkin Institute of Electrochemistry of the Academy of Sciences of the USSR. In 1992 he received Ph.D. He studied photoelectrical phenomena in polymer systems. Currently he is engaged in the investigation of charge carrier transport in novel polymer and low-weight organic systems and he has a position as a senior researcher at the Frumkin Institute of Electrochemistry of the Russian Academy of Sciences. ca.50 patents and publications