

A New Electron-transport Active Compound: 3,5-Dimethyl-3',5'-di-*t*-butyl-4,4'-diphenquinone

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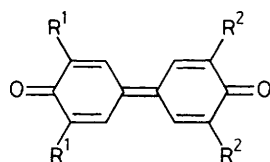
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A new electron acceptor having high polymer-compatibility, 3,5-dimethyl-3',5'-di-*t*-butyl-4,4'-diphenquinone, has been found to exhibit excellent electron mobility in its molecularly dispersed polymeric films.

Molecularly dispersed polymeric films of low-molecular-weight compounds have received much attention as a class of charge carrier transporting organic materials. Particularly, the polymer films doped with electron donors such as aromatic amine and hydrazone derivatives have been widely utilized as the hole transport materials in practical organic photoreceptors for electrophotography. On the other hand, electron acceptors are expected potentially to have electron transporting ability, whereas only a few such electron acceptors have been reported so far.¹⁻⁵ The electron mobility of their molecularly dispersed polymeric films, however, has not reached the order for the practical use (*e.g.*, 10^{-4} — 10^{-6} cm² V⁻¹ s⁻¹) because of their inferior charge transporting nature and low compatibility with conventional binder polymers to form homogeneous films. Only one exception has appeared in TNF (2,4,7-trinitro-9-fluorenone) complexed with PVK (poly-*N*-vinylcarbazole).^{1,2} It is attractive to develop electron transport materials as a counterpart of hole transport materials which are already in practical use. In general, however, most electron acceptors are characterized

by their poor solvent solubility and/or low compatibility with binder polymers. Therefore, electron acceptors for this function should be developed taking high polymer-compatibility as well as their excellent charge transporting nature into consideration.

Recently, we have found that 3,5,3',5'-tetra-alkyl-4,4'-diphenquinones, a family of electron acceptors, are capable of transporting negative charge. The symmetrically substituted diphenquinones with four identical alkyl groups, however, showed a poor polymer-compatibility of only 25 wt% (maximum) with limited binder polymers, resulting in low electron mobilities. In this communication, we report a new and unique member of this family, 3,5-dimethyl-3',5'-di-*t*-butyl-4,4'-diphenquinone (**1**), with unsymmetrical substitution of different alkyl groups, which provides high polymer-compatibility up to 80 wt% without appearance of microcrystals in its solvent cast films. The film gives excellent electron drift mobility of near 10^{-5} cm² V⁻¹ s⁻¹, which is higher than for any other molecularly doped polymeric materials reported so far.



- (1) $R^1 = \text{Me}$, $R^2 = \text{Bu}^t$
 (2) $R^1 = R^2 = \text{Me}$
 (3) $R^1 = R^2 = \text{Bu}^t$

A new diphenoquinone derivative (**1**) with two kinds of alkyl substituents, methyl and *t*-butyl, was synthesized by the oxidative coupling of a mixture of 2,6-dimethylphenol and 2,6-di-*t*-butylphenol referring to the method described in the literature.⁶ The low-symmetry product (**1**) was separated from the symmetrical by-products (**2**) and (**3**) by column chromatography on silica gel with dichloromethane as eluant and recrystallized from hexane to give yellowish red needles, m.p. 180–181 °C; λ_{max} (CH_2Cl_2) 422 nm.

The compound (**1**) exhibited very high solubility and polymer-compatibility compared with other symmetrically substituted diphenoquinones, (**2**) and (**3**). Using the ordinary solvent-cast technique, homogeneous films of (**1**) in polycarbonate (PC-Z, Mitsubisi Gas Chemicals)[†] were easily obtained without appearance of microcrystals even at high concentration (80 wt%), while (**3**) was limited to up to 25 wt% in PC-Z and (**2**) was hardly soluble in the casting solvents, *e.g.*, tetrahydrofuran, dichloromethane, and benzene. The diphenoquinone (**1**) also exhibited compatibility of more than 50 wt% with other common binder polymers: polyvinylbutyral, polyester, polyvinylchloride, and polystyrene. The dispersed polymer films of (**1**) were stable and showed no signs of crystallization over several months. We believe that such high solubility and polymer-compatibility of (**1**) have emerged from its lower symmetrical substitution, which reduces the cohesive force between the molecules. This is implied by the fact that the m.p. of (**1**) is much lower than those of (**2**) and (**3**), 216–218 and 245–247 °C, respectively.

For electron transport, the compounds are required to have sufficient electron affinity, since this process is considered to be a chain of redox processes between neutral and anion-radical molecules. The cyclic voltammogram of (**1**) in aceto-

nitrile exhibited a reversible reduction wave with a half-wave reduction potential of -0.48 V vs. standard calomel electrode (SCE), which is as low as -0.42 V in TNF.⁷

Thus, the diphenoquinone (**1**) was found to possess good polymer-compatibility and sufficient electron affinity as mentioned above. The electron transport properties of (**1**) were examined by the standard time-of-flight method using a nitrogen gas laser pulse. The polycarbonate films incorporating (**1**) in more than *ca.* 20 wt% showed well-defined transient photocurrents due to the photogenerated electrons passing through the sample films. As a typical electron mobility, the value of $2 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was obtained in 50 wt% loaded PC-Z film under an applied field of $5 \times 10^5 \text{ V cm}^{-1}$ at room temperature, although the mobility in the dispersed films depends on the dopant concentration, field, and temperature. This value is about one order higher than for TNF¹ under the same conditions, indicating that (**1**) is superior to TNF in electron transporting nature. The electron mobility of $2 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is also comparable to the hole mobilities of the hydrazone derivatives which are used practically as the hole transport materials in electrophotographic photoreceptors. From the temperature dependence of the mobilities, the activation energy for the hopping conduction was found to be 0.32 eV, which is quite small compared with 0.51 eV for the case of TNF.¹ It should be noticed here that at the maximum loading, 80 wt%, the electron mobility attained the order of $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. At present, this is the best data for organic electron transport materials of molecular dispersion. The details of the electron transport properties of 3,5,3',5'-tetraalkyl-4,4'-diphenoquinones will be presented in the forthcoming full paper.

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[†] Polycarbonate derived from 4,4'-cyclohexylidenebisphenol.