mT. However, this assignment is tentative and further measurements are in progress for confirmation.

These results demonstrate that enough main-chain scissions occur in the fracture of amine-cured epoxies so that the resulting radicals are detectable and identifiable by standard EPR techniques. Moreover, since some of these radicals are primary radicals they indicate the molecular failure sites where the chain scissions occur.

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I. M. Brown* and T. C. Sandreczki

McDonnell Douglas Research Laboratories
St. Louis, Missouri 63166

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Improved Hole Mobility of Polyacrylate Having a Carbazole Chromophore

Carrier mobility and photogeneration efficiency are essential factors in the performance of photoconductors.[1] Although organic photoconductors have certain advantageous characteristics, they are inferior to inorganic ones in both these properties, particularly carrier mobility.[2] Molecularly doped polymers are widely employed in both research[3-6] and practical uses.[7] In most cases, they exhibit higher carrier mobility than corresponding pendant-type polymers[8,9] except poly(*N*-carbazolylpropylene oxide).[10]

Polyacrylates and polymethacrylates containing adequate chromophores are good candidates for carrier transport materials with high mobility, since their stereoregularity can be controlled by the use of proper catalyst systems.[11] In the previous paper,[12] it was demonstrated that poly(2-*N*-carbazolylethyl methacrylate) has a carrier mobility similar to that of poly(*N*-vinylcarbazole) (PVK) despite its lower chromophore content, and we speculated that this is due to the ease of molecular motion of the carbazole moiety. Since the T_g of poly(2-*N*-carbazolylethyl methacrylate) is 155 °C, side-chain relaxation below the T_g was believed responsible for the enhanced molecular motion. Since this relaxation is known to occur at lower temperatures in polyacrylates,[13] we have measured hole transport characteristics of poly(2-*N*-carbazolylethyl acrylate) and here report that this polymer shows a hole drift mobility one order of magnitude higher than that of the corresponding polymethacrylate.

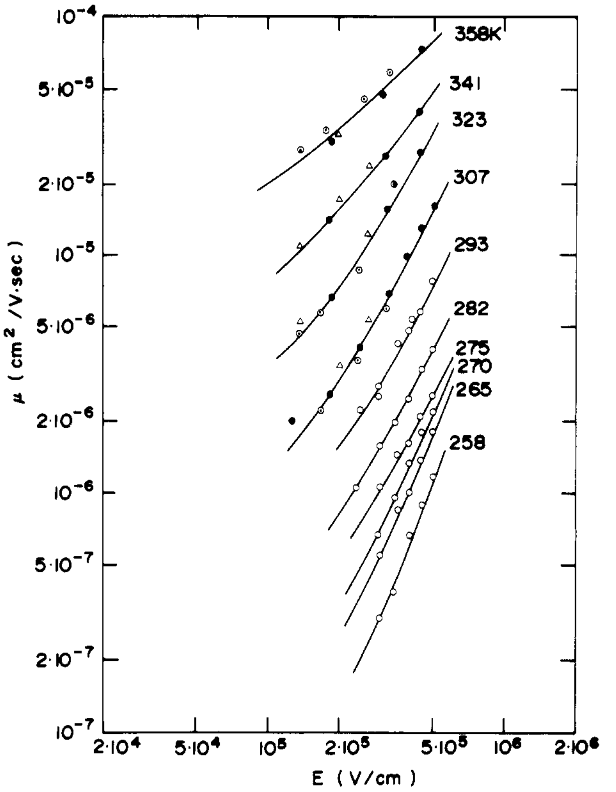

Figure 1. Electric field dependence of hole drift mobilities of poly(2-*N*-carbazolylethyl acrylate) at different temperatures. Thickness of polymer films was 16 (●), 10 (○), 6 (⊙), and 3 μm (△).

The polymer ($M_w = 5.6 \times 10^4$) was prepared by polymerization of 2-*N*-carbazolylethyl acrylate[14] in benzene (60 °C for 3 days; yield, 87%) using α,α'-azobis(isobutyronitrile) (0.5 mol %) as an initiator followed by three reprecipitations from methylene chloride solution with methanol. The hole drift mobility was determined by the time-of-flight method[12] using an 8-μs light pulse (435 nm) as incident light on layered samples composed of a thin polymer film deposited on an aluminum substrate from chlorobenzene solution at 40 °C[16] with a thin layer of a-Se deposited on the surface of the film and attached with a translucent top gold electrode. The carrier injection efficiency was measured by the photoinduced discharge method on similar layered samples without a top electrode at 450 nm.[17]

The photocurrent exhibited a very fast initial transient due to the transport of holes in the a-Se layer[18] followed by a well-defined plateau and then a long tail. The transit time was defined as the time at which the plateau and the tail intersected. For a 3-μm specimen, the transient current was dispersive and the transit time was evaluated from the shoulder of the plot of log (photocurrent) vs. log (time). Hole mobility was estimated conventionally from the transit time.

Hole drift mobility measured at various temperatures was strongly dependent on the applied electrical field, as commonly observed in disordered materials (Figure 1). The sample-thickness dependence was not prominent. It is noted that the room-temperature mobilities (at 293 K) are considerably greater than those of the corresponding polymethacrylate and PVK (at 295 K).[8]

For hopping transport among a set of localized sites, the mobility correlates with the average separation between

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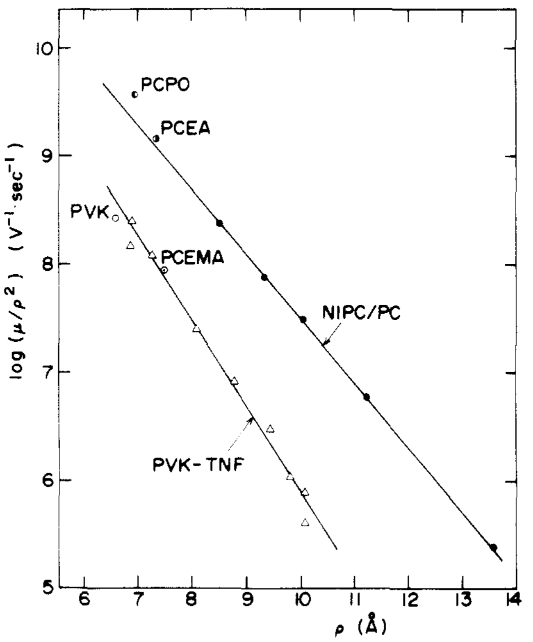

Figure 2. Comparison of room-temperature hole drift mobilities of hopping systems composed of carbazole chromophores at 5×10^5 V/cm in the μ/ρ^2 vs. ρ diagram. PVK (○), poly(*N*-vinylcarbazole); PCPO (◐), poly(*N*-carbazolylpropylene oxide);[10] PCEMA (⊙), poly(2-*N*-carbazolylethyl methacrylate);[12] PCEA (◑), poly(2-*N*-carbazolylethyl acrylate); NIPC/PC (●), *N*-isopropylcarbazole molecularly doped in bisphenol A polycarbonate;[3] PVK-TNF (△), poly(*N*-vinylcarbazole)-2,4,7-trinitrofluorenone charge-transfer complexes.[20]

sites (ρ) through the wave-function overlap factor; i.e., $\mu \propto \rho^2 \exp(-2\gamma\rho)$, where γ is the wave-function decay constant.[19] Then it is adequate to discuss the mobility data based on the (μ/ρ^2)–ρ plot.

The room-temperature mobility at 5×10^5 V/cm is compared with those of *N*-isopropylcarbazole (NIPC) molecularly doped with polycarbonate in Figure 2, where data for PVK, poly(*N*-carbazolylpropylene oxide),[10] the polymethacrylate,[12] and PVK-2,4,7-trinitrofluorenone (TNF) complexes[20] are also shown. It should be noted that the point for the polyacrylate lies on the line for NIPC/polycarbonate. The high mobility observed for the polyacrylate is thus a result of the decreased intersite separation. However, this is a significant result which demonstrates that it is possible to avoid the negative effect that has often been encountered when chromophores are incorporated in carrier transport systems through chemical bonds.[8,9]

The conventional Arrhenius plot of the data in Figure 1 comprised a set of apparently straight lines which intersected at a finite temperature as in the case of PVK-TNF.[20] The zero-field activation energy was estimated to be 0.55 eV from a plot of activation energy at different electric fields (E) vs. $E^{1/2}$. However, the more significant observation was that a set of straight lines was obtained when the logarithms of mobilities at different fields were plotted vs. T^{-2}, and further they converged to a common ordinate intercept (Figure 3). That is, the mobility obeys the relation $\mu(T) = \mu_0 \exp[-(T_0/T)^2]$.

This relation has recently been developed by both Monte Carlo simulations[21] and theoretical studies,[22] and has been corroborated for several amorphous organic hopping systems.[23,24] It indicated hopping across a Gaussian density-of-states distribution of width σ, where the disorder of site energies (diagonal disorder) plays a primary role. The parameter σ is related to T_0 by the equation $T_0 = K\sigma$, where K = 7400 K/eV. Only the two parameters μ_0 and σ characterize a transport system.

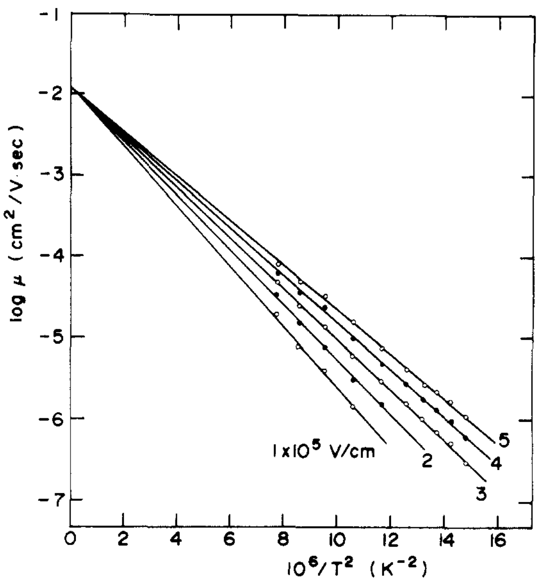

Figure 3. Plot of log μ vs. T^{-2} for the temperature dependence of the hole drift mobility for poly(2-*N*-carbazolylethyl acrylate) at different electric fields.

From the ordinate intercept of Figure 3, the preexponential factor μ_0 was determined to be 1.2×10^{-2} cm^2/(V s) for the polyacrylate. The parameter μ_0 is regarded as the hypothetical mobility of a hopping system with no disorder and is determined by the intrinsic nature of site molecules and the intersite distance (ρ). The above-obtained value for the polyacrylate (with ρ = 7.35 Å) seems realistic since it has been reported that μ_0 = 0.3 cm^2/(V s) for trap-free PVK (ρ = 6.6 Å)[25] and $\mu_0 = 5 \times 10^{-2}$ cm^2/(V s) for PVK-TNF (1:0.2) (ρ = 7.1 Å) and that γ is (1.3–1.8) $\times 10^{-8}$ cm^{-1}. From the ordinate intercept of the straight line given by plotting the T_0 values obtained at different fields vs. E, the zero-field value for T_0 was determined to be 949 K, which corresponds to a Gaussian width of 0.128 eV.

The difference in hole drift mobility of the acrylate and methacrylate polymers cannot be interpreted as a consequence of the slight differences in ρ (see Figure 2). Further, films of both polymers show no excimer fluorescence originating in the specific dimeric conformation,[26] which may act as a trapping center for holes in PVK.[27] Since both polymers were synthesized by simple radical polymerization, it seems unreasonable to expect large differences in tacticity between the two polymers, which could induce different degrees of order. It is to be expected that molecular mobilities are much lower in the polymethacrylate than in the polyacrylate from the fact that the T_g of the latter (105 °C) is considerably lower than that of the former (155 °C). Further, it is known that polyacrylates exhibit side-chain relaxations at lower temperatures than those of polymethacrylates.[13]

Since the present system is described by a model of hopping transport in a system subject to a Gaussian type of diagonal disorder, the difference in molecular motion should influence the Gaussian width σ. The direct coupling of molecular motion and carrier transport[28,29] seems implausible. The Gaussian width is determined by the fluctuation of polarization energy between a cation center and surrounding neutral molecules caused by spatial disorder.[23] Thus it is inferred that the extent of frozen-in

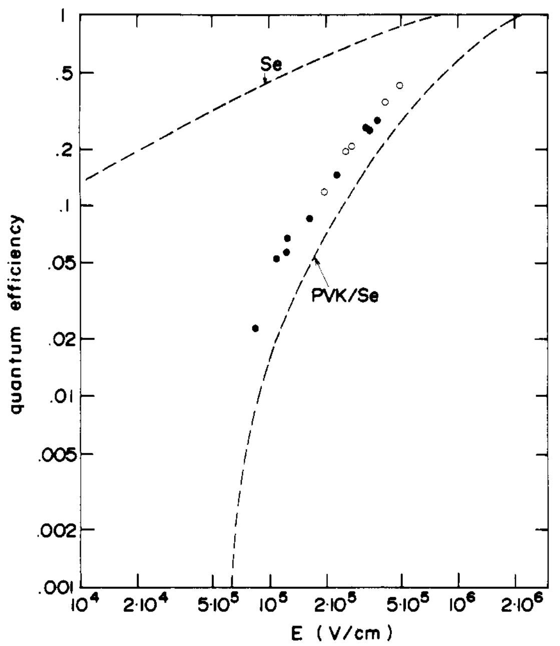

Figure 4. Apparent carrier injection efficiency from an a-Se layer into a layer of poly(2-*N*-carbazolylethyl acrylate) with the thickness of 14 (●) or 10 m (○). Xerographic gains of a-Se and 0.3-μm Se/12.5-μm PVK[30] are also shown for comparison.

disorder is smaller for the polyacrylate, in which the carbazole chromophores encounter less steric hindrance with the polymer backbone than in the polymethacrylate.

The hole injection efficiency from a-Se into the layer of the polyacrylate is depicted in Figure 4. The abrupt decrease of the apparent injection efficiency is a result of low carrier mobility of the polymer at low electric field; i.e., measurement were carried out while a transit was still proceeding in the polymer layer.[18] Compared with PVK/Se,[30] the falloff in the apparent injection efficiency occurs at a lower field, reflecting the high mobility of the present acrylate polymer.

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(17) The specimen was charged with a Colotron charger to an initial voltage. After a sample stage was moved into place under the surface-potential measuring probe, the decay of the voltage induced by irradiation with monochromatic light generated from a xenon tube through a monochromator was monitored with a Monroe isoelectric voltometer (Model 244), digitized with a transient converter and fed to an NEC PC-8800 microcomputer. Light intensity was adjusted sufficiently low to avoid a space-charge effect (<1 × 10^{12} photons/(cm^2 s) and the irradiation time was controlled with an electromagnetic shutter. All operations were controlled with the microcomputer. The injection efficiency (η) was evaluated from the initial photoinduced discharge rate $(\mathrm{d}V/\mathrm{d}t)_0$ by the relation $\eta = (\epsilon_0\epsilon/edI)(\mathrm{d}V/\mathrm{d}t)_0$, where ϵ_0 is the permittivity of vacuum, ϵ is the dielectric constant of the specimen (3.5), e is the electronic charge, d is the film thickness, and I is the incident photon flux.
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Ryuichi Oshima,* Toshiyuki Uryu, and Manabu Senō

Institute of Industrial Science, University of Tokyo
7-22-1, Roppongi, Minatoku, Tokyo 106, Japan

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A 2D-Exchange NMR Study of Very Slow Molecular Motions in Crystalline Poly(oxymethylene)

In NMR information about molecular motions is usually obtained by measurements of relaxation times T_1, T_2, $T_{1\rho}$, etc. These relaxation times are sensitive to relatively fast motions (T_1, MHz motions; $T_{1\rho}$, 10-100-kHz motions; T_2, ~1 kHz motions). Very slow molecular motions (1 kHz-0.01 Hz) can be investigated by the spin alignment technique developed by Spiess.[1] This last technique, however, has the disadvantage that partly deuterated samples are needed.