

slowly or even stored at 95 °K for 8 or 16 hours¹². The ordering of this small part of the ice seems to be an almost spontaneous occurrence as the temperature is lowered to about 120 °K. A lowering of the activation energy for the movement of the defects in the neighbourhood of the dopant molecule could be the cause. It would mean that the area around a foreign molecule is quickly reorientated as the temperature reaches the transition temperature but that the mechanism then changes to a much slower procedure of reorienting the ice by the migration of the defects in the undisturbed crystal. It seems that

in all the experiments so far the time required to reach more than only a few percent of order in the ice is far longer than the time normally available for these physical experiments.

Conclusion

Ice seems to possess a transition temperature near 120 °K at which it would become ordered during cooling if one would wait long enough. Doping the crystal catalyses the transition by lowering the activation energy for the mobility of the various defects in the neighbourhood of the dopant molecule.

Electroluminescence in Mylar Films

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Dedicated to Professor Dr. N. Riehl on his 70th birthday

Non-destructive electric breakdown through mylar films is associated with emission of an intense light flash. Within an active volume of about $4 \times 10^{-8} \text{ cm}^3$, $L \geq 10^9$ photons are generated during a current pulse. L is proportional to the number of transported charge carriers (electrons) and independent from sample thickness. The emission spectrum is a superposition of ordinary mylar fluorescence centered at 370 nm and impurity bands at longer wavelengths. Interpretation is given in terms of acceleration of injected electrons within the positive cathodic spacecharge zone giving rise to both impact excitation and ionization, predominantly involving guest molecules.

Introduction

Since the discovery of electroluminescence in inorganic semiconductors and insulators¹ many papers have appeared reporting on the observation of the effect also with organic materials. BERNANOSE et al.² among others³ have shown that organic scintillators, when embedded in a thin polymer matrix, can be excited in the same way by a periodic electric field as inorganic phosphors. Later on, however, SHORT and HERCULES⁴ were able to demonstrate that in most cases the observed emission

bands can be identified with the second positive series of nitrogen, which is the spectrum obtained from the positive column of discharge tubes containing air or N₂ at low pressure. Thus the effect of organic electroluminescence could be traced back to spurious glow discharge taking place within microcavities of the matrix which contain small amounts of N₂ encapsulated during sample preparation.

In general the absence of electroluminescence — the term should not be confused with recombination radiation emitted as a result of annihilation of a thermalized electron-hole pair — in organic materials is a re-

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¹ G. DESTRIAU, J. Chim. Phys. **33**, 587 [1936].

² A. BERNANOSE, M. CONTE, and P. VOUAUX, J. Chim. Phys. **50**, 64 [1953].

³ M. DERVENIZA, Nature **200**, 558 [1963].

⁴ G. D. SHORT and D. M. HERCULES, J. Amer. Chem. Soc. **87**, 1439 [1965].



sult of the extremely small bandwidth of the highest valence and lowest conduction band which does not allow electron or hole acceleration. This is a consequence of weak intermolecular coupling in these substances. Therefore RIEHL⁵ was not able to detect "true" electroluminescence in anthracene single crystals. Carrier acceleration required for impact excitation to take place is only possible if electron states in upper conduction bands can be populated which are much wider and possibly overlap. POPE et al.⁶ have interpreted the observation of fluorescence emission from crystalline anthracene under high field action in terms of electron injection from the contact into the second conduction band which is separated from the lowest conduction band by an energy gap of 0.6 eV⁷.

The purpose of the present paper is to demonstrate that in thin mylar films electron acceleration is possible at electric fields exceeding 5 MV cm^{-1} . Light emission observed in connection with non-destructive breakdown occurring at these field strengths^{8,9} is used as a probe. Emission partly originates from unspecified impurities. From the magnitude of the effect, however, glow-discharge within microcavities can be disregarded as the main source for light production.

Experimental

Commercial mylar (polyethyleneterephthalate)-films of the thicknesses 4, 6, 10 and 20μ were used for the investigation. Informative measurements were carried out with polystyrene films. The experimental setup was essentially the same as described previously⁸. The sample was placed between a tinoxid-coated glass anode and a cathode which usually consisted of a polished stainless steel ball, but which eventually was replaced by a small droplet of silver paste or an evaporated gold dot without effecting the results. The sample holder was mounted in a vacuum chamber with a glass window operated at a pressure $\leq 10^{-5}$ Torr. Measurements at 77°K could be performed after attaching the sample holder to a cold finger. Usually the sample was allowed to outgas several days before measurements were taken.

The electrical circuit is shown in Fig. 1. A negative potential V could be applied to the cathode by a high voltage power supply. A $10^{11} \Omega$ loading resistor was

chosen in order to ensure a time constant of about 10 s for the loading circuit. This proved to be necessary to control charge flow during breakdown⁸. It has been shown that as long as the capacitance $C_s + C_p$ is of the order $\leq 100 \text{ pF}$ nondestructive breakdown occurs if V exceeds a critical value. It causes a voltage drop ΔV across the sample. Usually $\Delta V/V = 0.1 \dots 0.5$, depending on capacitance and slightly on sample thickness. ΔV was measured with a static voltmeter. The transported charge $\Delta Q = (C_p + C_s) \Delta V = \int i dt$ was recorded in a ballistic way utilizing a Tektronix 502 A double beam oscilloscope. (The actual duration of the breakdown pulse is $5 \dots 100 \text{ ns}$ depending on $C_p + C_s$ and therefore much shorter than the time constant $R_{os} C_{os} \approx 5 \times 10^{-5} \text{ s}$ of the oscilloscope.)

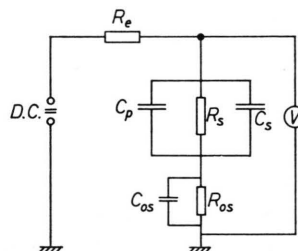


Fig. 1. Electrical Circuit. D.C. is the high voltage power supply, R_e the loading resistor ($10^{11} \Omega$), R_s the sample resistance, C_s the sample capacitance (typically 1 pF), C_p the cable capacitance of about 100 pF parallel to C_s , R_{os} and C_{os} oscilloscope input resistance and capacitance. V is the electrostatic voltmeter.

The integral intensity $\int I dt$ of the light pulse emitted during the breakdown event was recorded with a RCA 6655 photomultiplier which was connected to the second channel of the oscilloscope. For measurements of the decay time of $I(t)$ the time constant of the circuit was reduced by means of a $1 \text{ k}\Omega$ resistor parallel to the input resistance of the oscilloscope. Schott interference filters were used for crude spectral analysis of the emitted light.

For purpose of comparison also the emission spectrum of a mylar film under optical excitation was investigated. The sample was excited with the 302 nm line of a mercury high pressure lamp, spectrally isolated by a Beckman grating monochromator.

Results

When the electric field across the sample reaches a critical value F_1 , typically 3 MV cm^{-1} , non-destructive breakdown occurs, i. e. the sample resistivity decreases abruptly by many orders of magni-

⁵ N. RIEHL, Ann. Physik [6], **20**, 93 [1957].

⁶ M. SANO, M. POPE, and H. KALLMANN, J. Chem. Phys. **43**, 2920 [1965].

⁷ H. BÄSSLER, N. RIEHL, and G. VAUBEL, Mol. Cryst. **9**, 249 [1968].

⁸ N. RIEHL, H. BÄSSLER, S. HUNKLINGER, W. SPANNRING, and G. VAUBEL, Z. Angew. Physik **27**, 261 [1969].

⁹ H. BÄSSLER, N. RIEHL, and W. SPANNRING, Z. Angew. Physik **27**, 321 [1969].

tude and attains its original value after 100 ns or less. A subsequent breakdown can be initiated after the field has reached a value $F_2 = F_1 + \delta F_2$. In general the n -th breakdown occurs at $F_n = F_{n-1} + \delta F_n$. δF_n approaches zero for $n > 10$. For $n = 2$, $\delta F_n / F_n \approx 0.1$. The time delay between subsequent breakdown events is determined by the time constant of the loading circuit. The amount of charge ΔQ_n transported through the film increases with n and saturates for $n > 10$: $\Delta Q_{n>10} \approx 2 \Delta Q_1$. The electrostatic energy dissipated in the sample is $\Delta E_n = V_n C \Delta V_n = V_n \Delta Q_n$, where $V_n = F_n d$, d denoting the sample thickness. Hence $\Delta E_n / \Delta Q_n = V_n$. In other words, the energy dissipated in the film by a fixed amount of charge increases with the critical external breakdown field. Absolute values for ΔV_n are subject to considerable statistical fluctuations.

The essential observation which the present communication reports on is that non-destructive breakdown is accompanied by emission of a relatively intense light flash. Figure 2 shows that the inte-

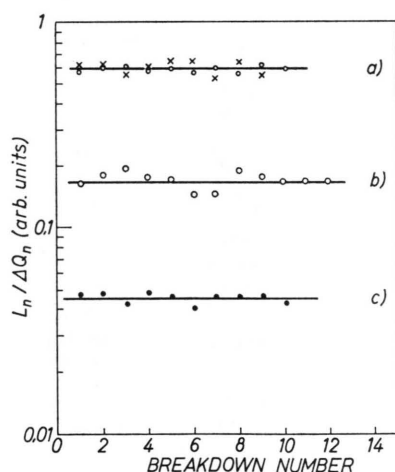


Fig. 2. Emission intensity normalized to the number of transported electrons as a function of the breakdown number. Curve a was taken with a neutral density filter, curve b with a 420 nm and curve c with an 548 nm interference filter (half-width of the filters about 15 nm). Values of curve a denoted by crosses refer to an experiment, in which the ordinary glass anode was replaced by a tin oxide-coated glass covered with a 500 Å evaporated silica layer.

grated intensity $L_n = \int I_n(t) dt$ is proportional to the transported charge ΔQ_n . It therefore decreases with ΔE_n : $(L_n / \Delta E_n) \sim (1 / V_n)$. The existence of a linear relationship between L_n and the number of transported charge carriers rather than their energy becomes even more evident by comparing L_n for films

of various thicknesses. Since ΔQ_n is independent of d , $L_n / \Delta Q_n$ must also be independent of d as long as only the number of carriers is important.

Table 1 shows that this indeed is observed. Implicitly these results contain the information that the light output does not depend on the time interval between subsequent breakdown events. Thus no chemical regeneration process can be involved.

Table 1. Light output at various film thicknesses.

d (μ)	F_1 (MV/cm)	L_n (rel. units)	$L_n / \Delta Q_n$ (rel. units)
4	3.6	1.0	2.3
6	3.1	1.3	2.4
10	2.9	0.9	2.1
20	2.5	1.2	2.5

Fig. 3 compares the emission spectra of mylar obtained under electrical and optical excitation conditions. Apparently the spectra are identical in the range 350 to 450 nm, where the emission properties

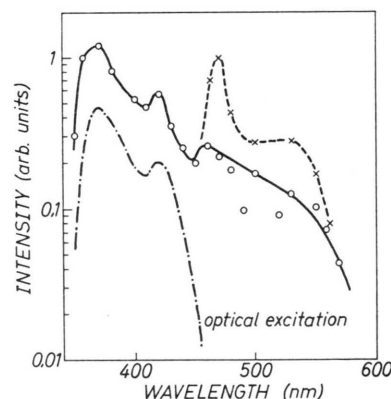


Fig. 3. Electroluminescence spectrum of mylar. The dashed curve was taken with a 10 μ film doped with naphthalene. For $\lambda < 460$ nm no difference between the doped and the undoped film is detectable. — · — · —: Mylar emission spectrum under optical excitation.

are dominated by the carbonyl group of the ethyleneterephthalate monomer unit. However, the electroluminescence spectrum extends to longer wavelengths. This is a common feature of this type of emission spectra and is indicative of impurity emission. The conclusion that emission in the spectral regions $\lambda < 450$ and > 450 nm originates from different species is supported by decay time studies: For $\lambda > 450$ nm the decay time of the light pulse is 2 μ s at roomtemperature and 3 μ s at 77°K. At 370 nm, where the short wavelength band has

its maximum, only an upper limit of 5×10^{-7} s can be given. The short wavelength emission can therefore be attributed to a transition from the lowest excited $n\pi^*$ singlet state of the monomer unit to the ground state.

With polystyrene films only impurity emission is detectable for $\lambda > 350$ nm. Its spectrum differs from mylar impurity emission.

In one series of experiments the mylar film was doped with naphthalene by embedding the sample into molten naphthalene ($T = 100^\circ\text{C}$) for one day. Assuming a diffusion coefficient for the naphthalene molecule of the order ¹⁰ of 10^{-12} cm² s⁻¹, a doping "depth" of $3\ \mu$ can be estimated. In this case evacuation of the breakdown chamber had to be accomplished within a short time (about 15 min) in order to minimize diffusion of naphthalene out of the film during the experiment. Although the experimental conditions, i.e. concentration and spatial distribution of the dopant, were not well defined in this set of experiments, it nevertheless came out clearly that the emission intensity of the doped film was increased by a factor of 3 to 6 near $\lambda = 470$ nm and that the decay time in this portion of the spectrum was drastically enhanced. Since the 0–0 transition of the naphthalene phosphorescence is centred at 467 nm, the additional emission near 470 nm is most likely to be attributed to radiative $T_1 \rightarrow S_0$ decay in the naphthalene guest molecules.

The total number of photons emitted per breakdown event can be estimated from the multiplier current taking into account the spectral sensitivity of the multiplier, the intensity distribution of the emission spectrum, and the geometric conditions. For undoped mylar films $L_1 = 3 \times 10^9$ quanta per pulse is obtained. The uncertainty is at least a factor of 2. Losses caused by total reflexion of the emitted light at the film surface are neglected. Comparing this figure with the number of transported electrons $\Delta Q_1/e \cong 4 \times 10^{11}$ per pulse gives the total electroluminescence quantum yield $\eta_{\text{el, tot}} = e L_n / \Delta Q_n \approx 10^{-2}$. The quantum yield for emission in the spectral range 350 to 450 nm equals $(2/3)\eta_{\text{el, tot}}$. Numerically the quantum efficiency measured under optical excitation conditions is about the same: $\eta_{\text{opt}} \approx 10^{-2}$ emitted photons per absorbed photon.

Interpretation

Two mechanisms for generation of excited states during non-destructive breakdown can be envisaged: (1) Recombination between electrons injected from the cathode and holes trapped in the polymer film; (2) Charge acceleration within the film leading to impact excitation. The latter mechanism subdivides into two groups: (2 a) Electron avalanche formation within the bulk of the polymer film and (2 b) glow discharge within microcavities.

Process (1) must be considered since it has been shown⁸ that the occurrence of non-destructive breakdown is due to cold-emission of electrons from the cathode under the combined action of the external field and the field of a positive cathodic spacecharge layer. In the initial breakdown stage the spacecharge field amounts to $F_{\text{sc}} \approx 2 \times 10^6$ V cm⁻¹ which according to $n = \epsilon \epsilon_0 F_{\text{sc}}$ is equivalent to an area density of $n = 3 \times 10^{12}$ holes per cm². Therefore $N \approx 10^9$ trapped holes are stored in the breakdown channel which has an area $\leq 4 \times 10^{-4}$ cm². This is less than the average number of emitted photons per event. Hence it is obvious, that carrier recombination cannot account for the observed light emission. The unimportance of recombination between electrons and holes injected from the counterelectrode is demonstrated by the failure to influence light emission by covering the anode by a 500 Å evaporated silica layer which blocks hole injection completely (see Fig. 2).

Glow discharge involving N₂ molecules as the predominant source for light production can also be disregarded on numerical grounds. Assuming a thickness of $1\ \mu$ for the cathodic high field zone, a volume density $N_{\text{ph}} = 5 \times 10^{16}$ photons emitted per cm³ and event follows for the spectral region in which intrinsic mylar emission prevails. Within the framework of the glow-discharge concept host emission is caused by reabsorption of light emitted by excited gas molecules, particularly N₂⁺, in the discharge cavities. Since the fluorescence efficiency of mylar η_{opt} is 10^{-2} , 5×10^{18} N₂⁺ molecules per cm³ are necessary to explain the observed emission intensity. This is only a factor of 4 less than the molecular density of N₂ at atmospheric pressure and roomtemperature, apparently an unreasonable result.

The inapplicability of the glowdischarge concept is further demonstrated by comparing the present results with literature data on electroluminescence

¹⁰ J. N. SHERWOOD, Crystal Growth 839 [1967].

of mylar at lower than breakdown fields. Extrapolation of the intensity versus field curve reported by HARTMANN and ARMSTRONG¹¹, which *could* be explained on the basis of the glow discharge hypothesis and which therefore represent an upper limit for glow discharge radiation, to breakdown conditions yields emission intensities which are 4 to 5 orders of magnitude lower than the presently observed ones.

Therefore we conclude that the results reported herein can only be explained in satisfactory manner by assuming electron acceleration within the lattice of the polymer film itself. The fact that about 30 percent of the observed emission originates from impurities which do not — or at least with much lower efficiency — emit under optical excitation is not in conflict with this interpretation, since (1) hot electrons are predominantly scattered inelastically at impurity sites and (2) their energy distribution function will certainly have its maximum at an energy below the mylar singlet excitation energy which is about 3.5 eV. This is supported by the observation of the phosphorescence of naphthalene molecules embedded in the mylar host. It is known that the triplet state is effectively excited by electron impact. The fact that despite the low phosphorescence quantum yield guest phosphorescence is almost as intense as singlet emission from mylar demonstrates the dominating influence of impurities with lower lying optical levels on electroluminescence^{11a}.

It is easy to show that the hot-electron model is in accordance with the finding that the number of emitted photons is proportional to the number of transported charge carriers rather than to their total electrostatic energy. It further confirms the interpretation of nondestructive breakdown previously presented⁹. As already mentioned, previous electric experiments have supported the existence of a positive cathodic spacecharge region, the thickness of which is independent of the sample thickness. Since the electron acceleration probability rises superlinearly with the electric field, the impact excitation

probability α_{exc} will have its maximum value near the cathode. Thus light production is most effective within a cathodic zone $a < d$, being the sample thickness. This explains the independence of the emission intensity from the sample thickness. The observation of identical breakdown characteristics with varying d necessarily implies that the potential distribution within this spacecharge layer is also independent from the actual sample thickness. Therefore a fixed number of injected electrons will deposit a fixed amount of energy to the spacecharge zone, which partly is convertible into optical excitation energy. The major and of course thickness dependent part of the total electrostatic energy of the electrons is converted into heat in the low-field bulk portion of the sample. Thus the proportionality $L_n \sim \Delta Q_n$ is a consequence of the hot electron model.

Previously 3 observations have led to the assumption of impact ionization during non-destructive breakdown⁸ (1) The cross-section for electron-hole recombination is much smaller than estimated under strong scattering conditions¹²; (2) the spacecharge field increases during the initial breakdown step; (3) the electron mobility is typical for hot electrons. The observation of impact excitation represents a crucial confirmation of the electron avalanche model since it is inevitably coupled with the occurrence of impact ionization.

A numerical estimate yields reasonable figures for the excitation probability α that an electron on its way to the anode creates an optically excited state: $\alpha_{\text{opt, UV}} \approx 1$ for excitation of the mylar monomer unit and $\alpha_{\text{opt, imp}} \gg 1$ for impurity excitation. This number may be compared with an impact ionization probability $\alpha_{\text{ion}} \approx 0.8$.

As a physical basis for hot electron generation in an organic material with weak intermolecular coupling we suggest electron acceleration within the polymer molecules rather than between the molecules⁸.

¹¹ W. A. HARTMAN and H. L. ARMSTRONG, J. Appl. Phys. **38**, 2393 [1967].

^{11a} The naphthalene triplet state could also be populated by energy transfer from a $n\pi^*$ host triplet state, but not by reabsorption effects.

¹² M. SILVER and R. SHARMA, J. Chem. Phys. **46**, 692 [1967].