

Slow Luminescence Emission from Polymers with a Hyperbolic Decay Law. A Survey of Commercial Materials With an Apparatus of Wide Aperture

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Synopsis

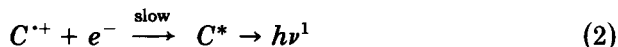
A survey of 98 commercial polymers with an apparatus responding to a sample area of 20 cm² revealed luminescence in about a third of them with a characteristic, hyperbolic decay extending over several minutes after brief irradiation with an incandescent source. The time dependence of the intensity was described well by the Debye-Edwards equation, of the form $I = At^{-m}$, with m between 0.67 and 1.17 except for polyvinylcarbazole, with $m = 1.76$. In a few cases studied in more detail, the emission could be stimulated by wavelengths extending into the visible region, showed a negligible temperature dependence (6–40°C), and was little affected by removal of oxygen or water from the atmosphere around the samples. The source of the emission is ascribed to charge recombination of photoejected electrons from chromophores in the polymer structure or (in most cases) present as adventitious impurities which were not extractable in two cases. Nylon 6, which showed little emission alone, gave well-defined hyperbolic curves after heating in air or after addition of the fluorescent dye Benzoxanthene Yellow H2495.

INTRODUCTION

Some time ago one of us¹ pointed out that weak light emission, stimulated by an incandescent source, was observed on a time scale of minutes from a variety of organic materials and could be fitted to an expression $1/I \equiv dt/dh\nu = kt$ for $t > 0$, corresponding to the Debye-Edwards equation² with $m = 1$. The parameters describing the decay have been empirically correlated in unpublished studies carried out by one of us (G. D. M.) to the composition, processing variables (e.g., degree of cure), age, or state of deterioration of edible or fabricated materials. Since those studies were largely proprietary and involved complicated systems, we have undertaken a survey of single-component polymers in order to establish the scope of the luminescence. In addition to empirical applications, the nonexponential emission is important because it will contribute an apparent background signal to the exponential luminescence decay that is usually sought in polymers at much shorter observation times. A third interest in the phenomenon arises from its possible association with single electron transfer processes leading to polymer oxidation.³

We have used the term charge recombination luminescence to describe the emission by analogy to a number of other studies which have shown that a power function describes phenomena associated with diffusive electron-cation

recombination⁴⁻⁸:



where C = chromophore and C^* = electronically excited C . We prefer the term Debye-Edwards luminescence (DEL) to describe the curves, since these workers were among the first to describe the hyperbolic decay curves in terms of electron recombination.

EXPERIMENTAL

The apparatus (Fig. 1) was a very simple device which allowed one to irradiate a thin layer of polymer with a conventional, 100 W incandescent light. A 1 cm layer of water in a Pyrex dish absorbed a large portion of the IR emission, and direct measurement of the sample surface with a thermocouple showed that the transmitted photons of all wavelengths produced no significant temperature rise. An irradiation time of 10.0 s was found to be sufficient to give a photostationary steady state. Following the irradiation, the sample was manually slid into a light-tight chamber under a photomultiplier tube-housing and the decay recorded for several minutes. This procedure gave good reproducibility ($m \pm 0.05, \ln A \pm 0.2$), and the irradiating source was more stable and less damaging to samples than conventional laboratory lamps of higher power.

Data were collected in the photon-counting mode with a computer system described earlier.⁹ Parameters for the Debye-Edwards law were made by optimizing the F -statistic of the least-squares analysis of log-log plots by subtracting out a constant background counting rate which was usually small in comparison to the recombination luminescence. The values of $\ln A$ (intercept) and m (-1 *slope) so obtained are given in Table I. The magnitude of A so evaluated depends on the sampling time interval and other factors (see Appendix).

For the experiments at 6°C the entire apparatus was moved into a cold room at that temperature. For experiments at 40°C, two horizontal 150 W heaters were attached to the sides of sliding device, and the input voltage was adjusted to give the desired temperature.

Polymer samples were taken from a collection available from SP2, Inc. (Kit no. 205) and examined initially without further treatment. A few samples from other sources are indicated parenthetically or in footnotes in Table I. Polyvinylcarbazole (PVK) was purchased from Polysciences, Inc. All samples were in the form of powders or granules. A sample of nylon 6 (4.9 g) was allowed to stand in a methanol solution $5.95 \times 10^{-6}M$ in Benzoxanthene Yellow H2495 (Hoechst 2495, from Aldrich Chemical Co.), the solvent was decanted, and the yellow polymer was dried. The concentration of the dye in the polymer was calculated as $7.9 \times 10^{-4}\%$ from the change in optical density of the methanol solution.

TABLE I
Charge-Recombination Parameters for Polymers

Polymer	Time interval (s)		Background photons	Δt (s)	m	pm^a	$\ln A$	$p \ln A^a$	r^2	Photons detected	
	From	To								T_{30}	T_{300}
	Variables fitted to equation $\log(I \cdot \Delta t) = \log A - m \log(t/\Delta t)$										
1. Alginic acid, sodium salt	10	600	100	5	0.924	0.02	11.323	0.006	0.9956	3160	375
2. Ethyl cellulose	21	600	100	3	0.823	0.1	9.234	0.02	0.9503	400	75
3. Hydroxybutyl (8%) methyl (20%) cellulose	35	600	125	5	0.814	0.05	10.732	0.01	0.9626	2130	325
4. Hydroxypropyl Cellulose	45	600	100	5	0.903	0.05	11.036	0.01	0.9616	2460	310
5. Hydroxypropyl (10%) methyl (30%) cellulose	55	600	100	5	0.781	0.05	11.311	0.009	0.9792	4030	670
6. Methyl cellulose	65	600	100	5	0.846	0.04	11.396	0.009	0.9813	3900	560
7. Nylon 6/6	20	600	100	5	1.021	0.08	10.189	0.02	0.9865	850	80
8. Nylon 6/9	20	600	125	5	0.942	0.06	10.413	0.015	0.9906	1230	140
9. Nylon 6/10	40	600	100	5	1.015	0.04	11.087	0.01	0.9911	2120	180
10. Nylon 6/12	20	600	100	5	0.772	0.04	10.041	0.01	0.988	780	195
11. Nylon 6/T	20	600	75	5	0.951	0.13	8.926	0.03	0.9515	270	30
12. Nylon 11	40	600	110	5	0.973	0.04	11.297	0.009	0.9941	2820	300
13. Nylon 12	35	600	75	5	0.943	0.04	11.799	0.009	0.9926	4900	560
14. Phenoxy resin ^b	20	600	75	5	0.903	0.04	10.286	0.01	0.9881	1160	145
15a. Polyamide resin ^c	60	600	1000	5	0.733	0.05	11.968	0.01	0.9971	8500	1560
15b. Polyamide resin	55	600	300	5	0.682	0.02	11.892	0.005	0.9961	8500	1560
16a. Polycaprolactone	55	600	100	5	1.059	0.013	13.982	0.003	0.9976	35400	3080
16b. Polycaprolactone	55	600	700	5	1.098	0.03	14.189	0.007	0.9987	35400	3080

TABLE I (Continued from the previous page.)

Polymer	Time interval (s)		Background photons	Δt (s)	m	pm^a	$\ln A$	$p \ln A^a$	r^2	Photons detected	
	From	To								T_{30}	T_{300}
	Variables fitted to equation $\log(I \cdot \Delta t) = \log A - m \log(t/\Delta t)$										
17. Poly(<i>p</i> -phenylene ether sulphone)	12	120	40	1	0.969	0.03	12.006	0.007	0.9882	6060	650
18. Poly(phenylene sulfide)	14	240	60	2	0.981	0.02	12.268	0.006	0.9925	7470	800
19. Polysulfone resin ^d	24	240	50	3	1.167	0.03	12.368	0.008	0.9994	3340	370
20. Vinylidene chloride/(20%) acrylonitrile	40	600	50	5	0.876	0.02	11.568	0.006	0.9901	4410	600
21. Poly(N-vinylpyrrolidone)	12	360	50	3	0.852	0.06	9.289	0.014	0.9719	500	70
22. Poly(4-vinylpyridine)	15	3600	25	3	0.981	0.033	11.312	0.006	0.9891	2840	300
23. Polystyrene (emulsion)	15	600	50	5	0.693	0.083	8.096	0.02	0.9062	190	40
24. Soluble starch	15	400	30	5	0.68	0.10	7.594	0.027	0.8225	120	25
25. Poly(α -methylstyrene)	21	360	10	3	0.60	0.02	10.069	0.007	0.9698	2000	500
26. Albumin, egg powder	18	360	40	3	0.932	0.03	10.389	0.009	0.9867	1270	150
27. Soluble starch	18	360	50	3	0.951	0.13	8.792	0.03	0.9349	250	25
28. Starch potato powder	25	600	50	5	0.731	0.12	7.892	0.01	0.9267	140	27
29. Starch wheat powder	15	600	30	5	0.682	0.06	8.039	0.011	0.9315	180	38
30. Starch corn powder	25	600	25	5	0.866	0.05	9.548	0.02	0.9823	600	80
31. Corn starch (Argo)	25	600	70	5	0.87	0.07	9.392	0.02	0.9669	500	68
32. Polycarbonate resin (Dow)	10	600	100	5	0.78	0.10	8.73	0.03	0.9613	220	50
34. Styrene acrylonitrile (Dow)	20	600	100	5	0.89	0.04	10.38	0.011	0.9941	1310	170
35. Styrene maleic anhydride (Dow)	20	600	25	5	0.75	0.02	8.942	0.008	0.9805	265	70

^aPseudoerrors from evaluation of data from single decay.^bCopolymer of epichlorohydrin and bisphenol A (2,2-bis-(4-hydroxyphenyl)propane).^cNylon mixture.^dCopolymer from 4,4'-dichlorodiphenyl sulfone and bisphenol A.

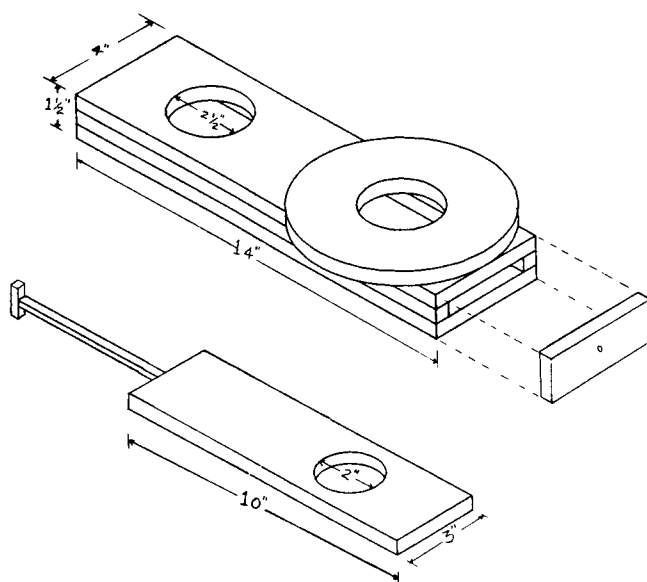


Fig. 1. Apparatus for detection of DEL.

An unsuccessful attempt was made to see unpaired spins by brief irradiation of a sample of nylon 11 in a 6 mm ID pyrex tube in the cavity of a Varian E9 electron spin resonance spectrometer. Unfiltered light from a 200 W high-pressure mercury lamp, focused with quartz lenses, was the excitation source for this experiment.

RESULTS

General Characteristics of DEL. The apparatus shown in Figure 1 is extremely simple and unsophisticated, and, in combination with the high precision of the photon counting capability, it is very useful for characterization of a wide variety of natural and artificial materials. The sliding device is actually unnecessary for many substances, since the generality of the phenomenon was recognized when attempts to measure thermal chemiluminescence in a number of samples were frustrated by a slowly decaying component of the emission, which was traced to stimulation by fluorescent room lights.

About a third of the samples that we studied showed luminescence persisting for minutes after irradiation. The nonexponential nature of the decay is apparent in the curve shapes in Figure 2, in which the optimized fits according to the Debye-Edwards equation are plotted for three representative examples.

There is some ambiguity in the selection of the parameters in Table I due to the presence of a background signal, which is composed of inherent tube noise (usually < 7 cps with a cold tube) and chemiluminescence emission from the polymer. This appeared to be a serious problem only when the DEL was very weak, or when color filters were used to filter the exciting or emitted light. In two cases (Table I, samples 15 and 16) the fit was equally good with background levels ranging over factors of 3 and 6, respectively. In most

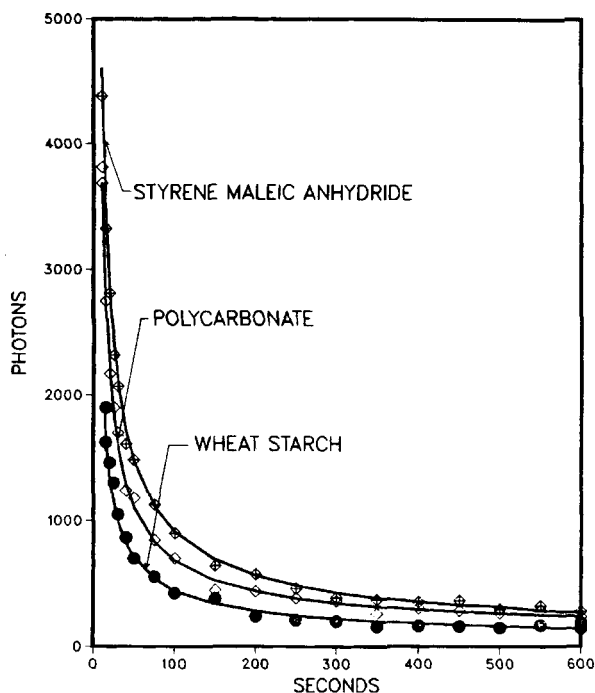


Fig. 2. Exemplary plots of DEL from polymers, as photons per 5-s interval vs. time. The fitted curves are drawn through (selected) experimental points.

examples, however, the best parameters led to a very close visual fit of the curve to the data, although systematic deviations were usually still apparent on examination of the residuals.

A list of polymers which did not show long-lived luminescence is given in Table II. In some cases we are able to detect the tail end of short-lived luminescence from these samples, but we were not able to collect sufficient data with this apparatus to distinguish between hyperbolic and exponential decay.

The mean exponential term of those given in Table I was 0.88 ± 0.13 . The calculated counting rates 30 s after the end of the irradiation varied from 120 (soluble starch) to 35,400 (polycaprolactone). Extrapolation to unit times ($I_0 \cong A/\Delta t$) gave an estimate for the steady state intensities of the DEL during irradiation, which vary over about two orders of magnitude in representative examples (Table III).

The effect of other variables was examined in a few cases. In Table IV, decay parameters are given for a sample of nylon 11 which was examined after successive irradiations in the usual way. Aside from minor systematic trends which may be due to characteristics of the irradiation system, the parameters are very similar.

We also selected four samples of representative polymers for the study of atmospheric dependence (Table V). The decay parameters showed minor differences in ambient air, dry air, or nitrogen.

TABLE II
Polymers Which Did Not Show Charge-Recombination Luminescence

1. Butyl methacrylate/isobutyl methacrylate copolymer	33. Poly(isobutyl methacrylate)
2. Cellulose acetate	34. Poly(methyl methacrylate)
3. Cellulose acetate butyrate	35. Poly(4-methyl-1-pentene), melt index 70
4. Cellulose propionate	36. Polypropylene isotactic
5. Cellulose sulfate, sodium salt	37. Polypropylene, chlorinated
6. Cellulose triacetate	38. Polystyrene
7. Ethylene/(20%) acrylic acid copolymer	39. Polytetrafluoroethylene
8. Ethylene/maleic anhydride copolymer	40. Poly(vinyl acetate)
9. Ethylene/(14, 18, 25, 28, 33, & 40%) vinyl acetate copolymer	41. Poly(vinyl alcohol) (88 & 100% hydrolyzed)
10. Methyl vinyl ether/(50%) maleic acid copolymer	42. Poly(vinyl butyral)
11. Methyl vinyl ether/(50%) maleic anhydride copolymer	43. Poly(vinyl chloride), inherent viscosity 1.26
12. Nylon 6 (polycaprolactam)	44. Poly(vinyl chloride) (1.8% carboxylated)
13. Polyacetal	45. Poly(vinyl fluoride)
14. Polyacrylamide	46. Poly(vinyl formal)
15. Polyacrylamide, carboxyl modified (low carboxyl content)	47. Poly(vinyl fluoride)
16. Polyacrylamide, carboxyl modified (high carboxyl content)	48. Poly(vinylidene fluoride)
17. Poly(acrylic acid)	49. Poly(<i>N</i> -vinylpyrrolidone)
18. Poly(1-butene), isotactic	50. Poly(vinyl stearate)
19. Poly(1,4-butylene terephthalate)	51. Rubber, chlorinated
20. Poly(butyl methacrylate)	52. Styrene/(20, 25, & 30%) acrylonitrile copolymer
21. Poly(1,4-cyclohexanedimethylene terephthalate)	53. Styrene/allyl alcohol copolymer (5.4-6.0% hydroxyl)
22. Poly(diallyl isophthalate)	54. Styrene/butadiene copolymer (ABA block, 30% styrene)
23. Poly(diallyl phthalate)	55. (85%) Styrene/butadiene copolymer
24. Poly(2,6-dimethyl- <i>p</i> -phenylene oxide)	56. (14%) Styrene/isoprene ABA block copolymer
25. Poly(4,4-dipropoxy-2,2-diphenylpropane fumarate)	57. (50%) Styrene/maleic anhydride copolymer
26. Polyethylene high density	58. Vinyl alcohol/(80%) vinyl butyral copolymer
27. Polyethylene, (25, 36, 42, & 48%) chlorinated	59. Vinyl chloride/(2, 10, 13, & 12%) vinyl acetate copolymer
28. Polyethylene, chlorosulfonated	60. (83%) vinyl chloride/(13%) vinyl acetate, (1% carboxylated)
29. Poly(ethylene oxide)	61. (80%) vinyl chloride/(14%) vinyl acetate/vinyl alcohol terpolymer
30. Polyethylene, oxidized (acid number 15 mg KOH/g)	62. Vinylidene chloride/vinyl chloride copolymer
31. Poly(ethylene terephthalate)	
32. Poly(ethyl methacrylate)	

The sample temperature had little systematic effect on the parameters derived from the curves of DEL obtained from three representative polymers (Table VI). The exponential term m showed less change than the values of A , which displayed slightly larger values at 25°C than at higher or lower temperatures. At lower temperatures, charge-recombination kinetics have been found to be independent of temperature in some cases^{4,5} and to show irreversible changes associated with annealing in others.⁶

Spectral Distribution. Color filters were used in separate, rough experiments to determine the significant wavelengths for excitation and emission. In

TABLE III
Calculated Initial Charge-Recombination Emission Following Irradiation

Polymer	<i>I</i> (counts/s)
Hydroxypropyl cellulose	12,400
Nylon 11	16,100
Nylon 12	26,600
Phenoxy Resin	5,900
Polycaprolactone	263,200

TABLE IV
Effect of Multiple Irradiations on DEL from Nylon 12

Nylon 12	Time interval (s)		Background photons	Δt (s)	<i>m</i>	<i>pm</i>	$\ln A$	<i>p</i> $\ln A$	<i>r</i> ²
	From	To							
After 1st irradiation	20	500	50	5	1.06	0.09	9.62	0.02	0.9709
2nd	20	500	75	5	1.05	0.12	9.56	0.03	0.9565
3rd	20	500	100	5	1.03	0.13	9.54	0.03	0.9743
4th	20	500	100	5	0.98	0.13	9.37	0.03	0.9750
5th	20	500	100	5	0.98	0.13	9.40	0.03	0.9722
After irradiation for 30 seconds	20	500	100	5	1.06	0.08	9.92	0.04	0.9689
Mean 1.03 ± 0.04							9.57 ± 0.20		

Table VII the exciting wavelengths for nylon 11 are seen to extend well into the visible region. The emitted light (Table VIII) appears to be concentrated between 400 and 490 nm, although there is some uncertainty because the manufacturer's curves for the photomultiplier tube indicate a decline in sensitivity from 20% at 400 nm to about 6.7% at 590 nm. In both types of experiments the effect of the filter should be only a diminution in the value of *A* from the subsequent data analysis (see appendix). This appears to be the case for the first three examples in Table VIII, but the last two filters removed so much light that there was a great deal of scatter in the data, and the fitted exponential term was anomalously low.

We attempted to extract chromophores from nylon 11 and the polysulfone resin with isopropanol-dichloromethane without success (Table IX). The polysulfone congealed into a hard lump during the extraction process, and was subsequently compression-molded into a sheet which showed DEL parameters virtually identical to those of the original resin.

Polyvinylcarbazole. After the original survey was completed, we became aware of work⁶ on laser-induced excitation in PVK, which gave emission corresponding to a power law over the range 0.05-lms. Unfortunately, it is not possible to calculate the value of the exponential term from the data given in this paper. Since photoconductivity via electron-hole formation is very well established for PVK, we examined a commercial sample in our apparatus and found the DEL to be the most intense by far of any polymer studied, with $\ln A = 17.99 \pm 0.02$ and $m = 1.792 \pm 0.007$ (average of 5 decays). In the previous work,⁶ signal averaging was necessary to obtain sufficient data for analysis. Although the source of the PVK, of course, may have been different

TABLE V
Effect of Atmosphere and Humidity on Charge-Recombination Luminescence from Polymers

Polymer/ atmosphere	Time interval (s)		Background photons	Δt (s)	Variables fitted to equation $\log(I \cdot \Delta t) = \log A - m \log(t/\Delta t)$				r^2
	From	To			m	pn	$\ln A$	$p \ln A$	
Ethylcellulose									
Air	15	500	50	5	0.792	0.162	7.573	0.043	0.8851
N ₂	15	500	50	5	0.828	0.240	7.161	0.064	0.7739
N ₂ + 20 torr H ₂ O	15	500	100	5	0.638	0.184	7.506	0.048	0.8818
Nylon 11									
Air	20	500	100	5	1.154	0.184	9.639	0.049	0.9578
N ₂	20	500	100	5	1.022	0.141	9.433	0.037	0.9738
After 3 h under N ₂	20	500	100	5	1.047	0.122	9.722	0.032	0.9794
Air + 20 torr H ₂ O	15	500	100	5	0.938	0.138	9.095	0.035	0.9443
N ₂ + 20 torr H ₂ O	20	500	100	5	1.053	0.136	9.624	0.036	0.9696
Polysulfone									
Air	20	500	100	5	1.164	0.057	11.123	0.051	0.9941
N ₂	20	500	100	5	1.193	0.052	11.412	0.014	0.993
After 3 h under N ₂	20	500	100	5	1.244	0.041	11.835	0.011	0.9971
Air + 20 torr water	20	500	100	5	1.091	0.037	11.375	0.01	0.9964
N ₂ + 20 torr water	20	500	100	5	1.297	0.056	11.711	0.015	0.9949
Experiments repeated after 30 days									
Air	20	500	25	5	1.132	0.036	10.384	0.009	0.992
N ₂	20	500	25	5	1.162	0.037	10.650	0.009	0.9912
N ₂ + 20 torr H ₂ O	20	500	25	5	1.160	0.031	10.756	0.008	0.9935
N ₂ + 20 torr water for 3 h	20	500	25	5	1.232	0.043	10.665	0.011	0.9899

TABLE VI
Effect of Temperature

Polymer	T (°C)	Time interval (s)		Background photons	Δt (s)	Variables fitted to equation $\log(I \cdot \Delta t) = \log A - m \log(t/\Delta t)$					r^2
		From	To			m	pm	ln A	p ln A		
Polysulfone	6	20	500	50	5	1.10	0.05	10.565	0.012	0.9895	
	25	20	600	50	5	1.22	0.08	10.455	0.020	0.9866	
Nylon 11	40	20	500	50	5	1.17	0.06	10.475	0.016	0.9904	
	6	20	500	50	5	0.887	0.07	8.996	0.019	0.9836	
Hydroxypropylcellulose	25	30	600	50	5	1.00	0.10	9.41	0.02	0.9624	
	40	20	500	50	5	0.94	0.07	9.317	0.018	0.984	
Hydroxypropylcellulose	6	20	500	50	5	0.83	0.10	8.45	0.026	0.9433	
	25	25	600	50	5	0.94	0.14	8.605	0.035	0.9044	
	40	20	500	50	5	0.867	0.1	8.585	0.025	0.9757	

TABLE VII
 Excitation of Nylon 11 through Cutoff Filters^a

λ^b	Filtered power (mW)	A	<i>m</i>	A_f/A_0
No filter	1.64	24477	1.09 ± 0.09	1.00
315	1.50	17154	1.00 ± 0.10	0.70
405	1.42	10615	0.96 ± 0.14	0.43
490	1.36	4359	0.90 ± 0.22	0.18
590	1.32	2565	0.91 ± 0.11	0.11

^a $\Delta t = 5$ s.^b50% transmittance value (nm)
 TABLE VIII
 Emission of Nylon 11 through Cutoff Filter^{a,b}

λ^c	A	<i>M</i>	A_f/A_0
No filter	24477	1.09 ± 0.09	1.00
315	22027	1.22 ± 0.15	0.90
405	20130	1.10 ± 0.13	0.82
490	13100	0.98 ± 0.12	0.54
590	2600	0.91 ± 0.11	0.11

^a Incident power 1.66 mW (water filter only).^b $\Delta t = 5$ s.^c50% transmittance value (nm).
 TABLE IX
 Effect of Extraction^a on DEL from Nylon 11 and Polysulfone

Nylon 12	Time interval		Background photons	Δt (s)	<i>m</i>	<i>pm</i>	$\ln A$	<i>p</i> $\ln A$	r^2
	From	To							
Nylon 11 before extraction	15	600	25	5	0.93	0.05	9.22	0.12	0.9753
Nylon 11 after extraction	15	600	25	5	0.91	0.05	9.13	0.12	0.9713
Polysulfone before extraction	15	600	50	5	1.22	0.07	10.45	0.02	0.9879
Polysulfone after extraction ^b	15	600	50	5	1.16	0.05	10.77	0.13	0.99

^a Refluxed with stirring for 1 h with a solution of 1 : 1 dichloromethane-isopropanol.^b Extracted polysulfone compression-molded to give a plaque.

than ours, the sensitivity of our apparatus is indicated by the observation of measurable DEL an hour after the original 10 s irradiation of this polymer.

DISCUSSION

Decay Kinetics. The hyperbolic decay curves from the polymer samples distinguish them from simple fluorescence or phosphorescence emission, although the actual DEL from the short-lived excited states may correspond to one of the latter. The exponential terms (*m*) in our experiments are in the same range as those found in other systems. Debye and Edwards, for instance, obtained values of *m* between 0.83 and 1.61 in UV-irradiated *p*-toluidine in frozen glasses.² The values for many of our polymers are close enough to unity

that the reciprocal formula applied earlier¹ would be satisfactory, although during initial attempts to use it in this study we found that a more general equation with an adjustable exponential term was preferable.

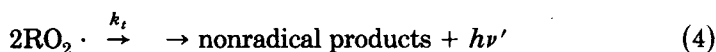
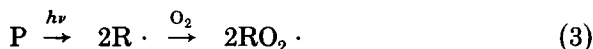
Stochastic models to account for the time dependence of hole-cation recombination processes have been advanced by a number of investigators recently.⁶⁻⁸ For instance, Stolzenberg et al.⁶ used a Monte Carlo simulation of geminate recombination with site hopping between i and j described by jump rates of

$$v_{ij} = v_0 e^{-2\gamma|r_{ij}|} e^{-(\epsilon_j - \epsilon_i)/kT}, \quad \epsilon_j > \epsilon_i$$

$$v_{ij} = v_0 e^{-2\gamma|r_{ij}|}, \quad \epsilon_j < \epsilon_i$$

With one particular set of parameters γ (wave function overlap) and v_0 , the simulated rate of electron-hole recombination followed a power function with $m = 1.13$, which is in the range of the exponential terms found in our study.

The use of short-wavelength excitation to produce a slowly decaying emission has been used previously by ourselves¹⁰ and others,¹¹ and ascribed without further evidence to *radical* recombination luminescence from an initially formed population of peroxy radicals:



(P = precursor, R = alkyl)

For a homogeneous initial distribution of radicals, the above mechanism leads to the prediction¹⁰ of a decay of the light intensity (I) according to the equation

$$1/I^{1/2} - 1/I_0^{1/2} = 2k_t t/f \quad (5)$$

where f is the efficiency factor and I_0 is the initial intensity. For large I_0 , the equation reduces to

$$I = (f^2/4k_d^2)t^{-2} = At^{-2} \quad (6)$$

In the presence of a background level of free-radical initiation giving rise to a nonstimulated luminescence I_∞ , the equation takes on a more complicated form:

$$\ln\left[\frac{(I_\infty^{1/2} + I^{1/2})}{(I^{1/2} - I_\infty^{1/2})}\right] = 4k_i[\text{In}]k_t t/f \\ - \ln\left[\frac{(I_0^{1/2} - I_\infty^{1/2})}{(I_\infty^{1/2} + I_0^{1/2})}\right] \quad (7)$$

where I_∞ is the "thermal" chemiluminescence produced by the background initiation rate $2k_i[\text{In}]$.

In our samples all but one of the exponential terms was below 1.2, which precludes the simple formula (4), and application of eq. (5) to several examples gave substantially worse fits to the data.

The temperature-independence of the parameters for the DE (Table VI) is an expected characteristic of a process involving diffusion of a small particle such as an electron, although we would expect *a priori* that significant differences might be found in polymers in temperature ranges where they undergo phase transitions, or above a critical temperature for electron transport as discussed by Hamill.⁴ The apparatus was designed only for a general survey, however, and we have not made a systematic study of this possibility over an extended range of temperature.

Bässler has predicted⁶ a temperature dependence of the recombination rate proportional to $e^{-(T_0/T)^2}$, where T_0 is the width of the assumed Gaussian distribution of trapping sites. The absence of a temperature dependence of the decay parameters in the experiments described in Table VI would therefore suggest relatively large values of T_0 .

We anticipated that water might plasticize the polar polymers and change the DEL decay characteristics, but the data in Table V do not show very pronounced difference between samples in humid vs. dry atmospheres. The decay characteristics in nitrogen vs. oxygen also do not show much change, although oxygen is an effective quencher for triplet states in polymers,¹² and can scavenge electrons to form superoxide ion with different diffusional characteristics. These results are consistent with trapping of photoejected electrons in relatively rigid or at least inaccessible sites of the polymer, followed by hopping between lattice sites in competition with slow recombination with the original cationic center as described.⁶

The emission from our samples in all cases was relatively weak, and the design of our apparatus with a wide collection area was necessary to measure the emission with satisfactory precision. The weakness of the signal, however, is partly a simple consequence of the slow decay. Although it is not possible to characterize the DEL fully because the concentrations and quantum yields of the emitting species are not known, we can estimate roughly from the data of Tables III, VII, and VIII that for nylon 11, about 5×10^{-7} of the incident photons in the active region of the spectrum are emitted as DEL. Since not all of the incident energy is absorbed by the sample, the quantum yield is probably larger than this value.

Nature of the Chromophore. We had expected that irradiation in the short end of the visible spectrum would be effective, but it was a little surprising that light even with wavelengths beyond 500 nm (< 57 kcal/mol) was able to give an easily measurable luminescence (Table VII). Several pieces of evidence indicate that adventitious chromophores are responsible for this DEL. First, except for poly(*p*-phenylene sulfide) and PVK, none of the polymers contain chromophoric groups in their normal repeating units which absorb appreciably in the visible region. Second, many polymers of similar structure appear in both the luminescing and nonluminescing categories (Tables I and II). In one instance (polycarbonate) the material from one source showed DEL but a sample from a different source did not. Third, the absence of DEL from polycaprolactam, in contrast to other polyamides, may be associated with its commercial synthesis by a ring opening rather than a

high-temperature condensation process. Finally, we have been able to stimulate long-lived luminescence (average of 5 decays: $\ln A = 7.61 \pm 0.2$, $m = 1.06 \pm 0.08$) in nylon 6 with a typical hyperbolic decay curve by addition of $7.9 \times 10^{-4}\%$ of a dibenzofuran dye which is known to complex strongly with proteins.

Several authors^{13,14} have proposed that photochemical damage to polymers is caused by adventitious chromophores including peroxidic and catalyst residues, polyaromatic hydrocarbons, and titanium compounds. While the connection between the chromophores responsible for degradation and the ones causing the DEL is not established, the latter cannot be aromatic hydrocarbons in nylon 11 and in the polysulfone, because we could not extract them with organic solvents. Peroxidic residues alone do not appear to be the chromophores because they are transparent in the visible region. It is unlikely that the same, added impurity would be responsible for the DEL in all of the samples we examined, since egg albumin and nylon 6/9, for instance, have obviously divergent origins, even though their hyperbolic decay parameters are quite similar.

Evidence that the chromophores in the nylon series are introduced by high-temperature processing was obtained by an experiment in which polycaprolactam was examined for DEL in the usual way after heating in air at 100°C for different times. A well-developed hyperbolic curve was apparent

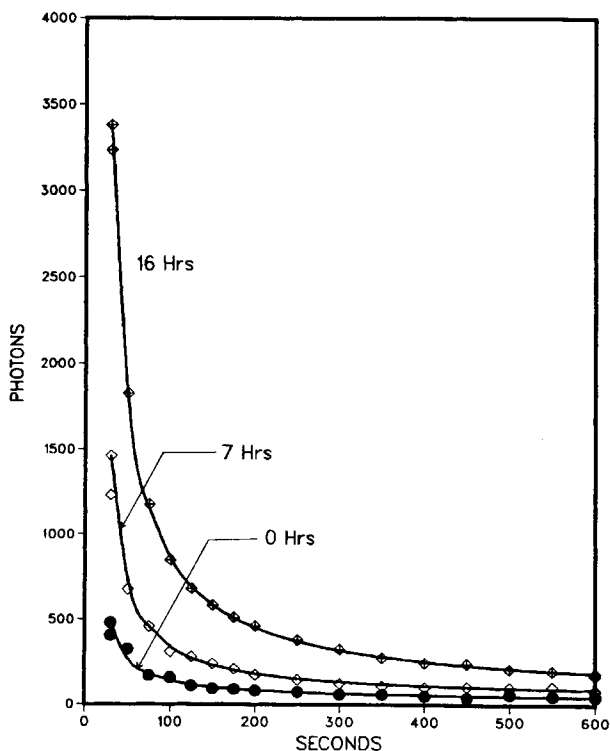


Fig. 3. DEL from poly(ϵ -caprolactam) at 25°C after heating at 100°C for the indicated times. The plotting is carried out as for Figure 2.

after 16 h, although the sample initially showed little luminescence (Fig. 3). A very slight discoloration was apparent in this sample after the heating period, when it was placed next to unheated material for comparison.

Electron Spin Resonance Experiment. The absence of a significant signal on irradiation of nylon 11 in an ESR cavity suggests that the number of unpaired spins is relatively small. From the data on nylon 11 in Table I and the integrated form of the Debye-Edwards equation, we estimate that the total number of photons emitted in the DEL experiment with this polymer was about 10^9 . Since the sample size in the ESR experiment was much smaller, it is not surprising if the free spins present were below the ESR detection limit of about 10^{13} , provided that the quantum yield of emission from the chromophore was above about 10^{-4} .

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APPENDIX

Cutoff Filters. For a decay of the form $I = At^{-m}$, interposing an optical filter between the sample and the detector will reduce the observed instantaneous intensity by a fraction f to a new value I' :

$$I' = fI = f dhw/dt = fAt^{-m} \quad (8)$$

Evaluation of the decay curve obtained with the filter in place will give a new preexponential factor $A' = fA$; hence $f = A'/A$ (Table VIII). The value of the slope of the log-log plot remains unchanged.

Similarly, self-absorption of emitted light from a sample, use of a detector with different sensitivity, or changing the distance from the sample to the detector will change the evaluated A factor but not m .

Normalization Correction. The data from our experiments were collected as the total photons during successive intervals Δt vs. the number of time intervals. In terms of the Debye expression given above, what we actually evaluated in the logarithmic transform of the raw data is therefore

$$\ln(I \cdot \Delta t) = \ln A' - m' \ln(t/\Delta t) \quad (9)$$

where I is approximated as an average intensity over the time interval. By comparison of this equation with the normalized form $\ln I = \ln A - m \ln t$, with I in counts/s and t in s, it can be shown that

$$m = m' \quad (10)$$

$$\ln A = \ln A' + (m' - 1) \ln \Delta t \quad (11)$$

Since the magnitude of A has no special significance, and is subject to proportionate increases due to the geometry of the apparatus and PMT response as well, the directly evaluated preexponential terms (i.e., A') are given in Table I without correction. The correction in any case is a small one and vanishes for $m = 1$.

References

1. G. D. Mendenhall, 174th American Chemical Society Meeting, Chicago, August 1977.
2. P. Debye and J. O. Edwards, *J. Chem. Phys.*, **20**, 236 (1952).
3. J. E. Pickett, in *Polymer Stabilization and Degradation*, P. P. Klemchuk, ed., ACS Symposium Series **280**, Am. Chem. Soc. Washington, DC, 1985, p. 313.

4. W. H. Hamill, *J. Phys. Chem.*, **82**, 2073 (1978).
5. F. Kieffer, C. Lapersonne-Meyer, and J. Rigand, *Int. J. Radiat. Phys. Chem.*, **6**, 79 (1974).
6. F. Stolzenberg, B. Ries, and H. Bäessler, *Chem. Phys. Lett.*, **116**, 73 (1985).
7. B. Ries, G. Schönherr, H. Bäessler, and M. Silver, *Phil. Mag.*, **B49**, 259 (1984).
8. R. Richert, B. Ries, and H. Bäessler, *Phil. Mag.*, **B49**, 55 (1984).
9. C. A. Ogle, S. W. Martin, M. P. Dziobak, M. W. Urban, and G. D. Mendenhall, *J. Org. Chem.*, **48**, 3728 (1983).
10. G. D. Mendenhall, *Ang. Chem. Int. Ed.*, **16**, 225-32 (1977).
11. G. A. George, *Dev. Polym. Degrad.*, **3**, 173 (1981).
12. G. Oster, N. Geacintov, and A. U. Khan, *Nature*, **196**, 1089 (1962).
13. D. J. Carlsson and D. M. Wiles, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C14**, 65 (1976).
14. J. S. Hargreaves and D. Phillips, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 1711 (1979).

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