

Monosubstituted derivatives of pyrene

Comparison of their spectral behaviour in solution and in polymer matrices

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Abstract

Spectral properties of monosubstituted derivatives of pyrene were compared in low viscosity solvents such as cyclohexane, chloroform, and methanol, in high viscosity solvents such as heptadecane and polybutene oil, in glassy polymer matrices above T_g (atactic polypropylene) and below T_g (polystyrene polymethyl methacrylate, polyvinylchloride), and in semi-crystalline low density polyethylene. The derivatives under study were: 1-pyrenylmethanol (I), benzyl-(1-pyrenylmethyl) ether (II), di(1-pyrenylmethyl) ether (III) and 4-(1-pyrenyl)butyl-(1-pyrenylmethyl) ether (IV). Absorption spectra of these probes were not influenced by environment. Emission spectra of III exhibited exclusively excimer emission in low viscosity solvents. Probe IV yielded mainly monomer emission. In viscous solvents and glassy polymer matrices above and below T_g , as well as in semi-crystalline polyethylene, monomer emission was exclusively observed for all probes. Distinct differences were observed in emission decay curves. Probes derived from pyrene with a bulky substituent exhibited biexponential decays with a short component (~ 10 ns) in viscous solvents and polymer matrices. In semi-crystalline polyethylene, the decay of monomer emission of all probes was monoexponential with a lifetime around 200 ns. © 2000 Elsevier Science S.A. All rights reserved.

Keyword: Pyrene

1. Introduction

Fluorescence probes based on chromophores of different types are widely used for monitoring various processes and functions on a microscopic level [1,2]. Pyrene and its substituted derivatives are chromophores of choice for this application because of the dependence of their vibrational structure on polarity [3], ability to form homo- and hetero-dimers in the excited state (excimers, exciplexes), and their long lifetimes in non-polar media (ca 400 ns). If these probes have a more complicated structure, aggregation can complicate their application to studies in the solid phase.

Previously [4–6], we have demonstrated that probes with pyrene having hydrophilic and hydrophobic parts can aggregate even at low concentrations depending on the method of preparation. These probes, under certain conditions, formed aggregates exhibiting excimer-like emission in pre-micellar solutions [4], in non-polar [5] and polar matrices [6]. The main feature of these aggregates is that they are stable during the lifetime of the excited states.

Bichromophoric probes, where chromophores are linked by a short chain, show dynamic excimer emission even at

high dilution in low viscosity isotropic solutions. In high viscosity solutions or in the solid phase, this emission is completely suppressed. The bichromophoric probes exhibiting excimer emission can provide insights into the micro-viscosity of semi-structured systems. For this purpose di(1-pyrenylmethyl) ether (III) was employed to measure the phase transitions and temperature dependence of a number of artificial phospholipid membrane systems [7].

In order to characterize the superstructure of semi-crystalline polyethylene (PE), the static and dynamic spectroscopic properties of four α,ω -di(1-pyrenyl)alkanes (P_nP where n , the number of methylene groups, is 3, 5, 7 or 12) were examined [8]. In isotropic media, nearly all P_nP provide emission from an intramolecular dynamically formed excimer [9]. A monochromophoric model for P_nP , 1-ethylpyrene, exhibited monoexponential decay ($\tau \sim 200$ ns) in both the films and in cyclohexane. Interchromophoric interactions in PE are intramolecular. Dynamic excimer formation occurred for P3P in low density PE. Static excimeric emission was observed in high density PE for P3P, and in low and high density PE for P5P. Especially in interfacial sites of PE films, the chromophoric groups of P_nP adopted specific conformations that are not detectable in normal isotropic or glassy media [8].

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It is evident that viscous media (liquids and amorphous solids) can influence the photophysical properties of monochromophoric or bichromophoric probes with hydrophobic or hydrophilic parts. In this paper, spectral properties of several monosubstituted pyrene derivatives with bulky groups containing additional chromophores are examined in media with different viscosity. The influence of environment on absorption and emission spectra and the dynamic decay of emission has been examined. It is clearly demonstrated that decay curves are the most sensitive parameter to follow medium changes.

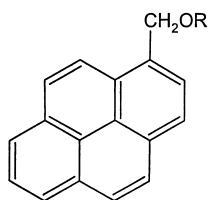
2. Experimental

The structures of the fluorescent probes used in this paper are shown in Scheme 1. 1-Pyrenylmethanol (I) and 4-(1-pyrenyl)butanol were from Aldrich-Chemie, Steinheim, FRG. They were used for syntheses of more complex probes following standard synthetic procedures. Anthracene and pyrene were zone refined (Lachema n.e., Brno, CR). Methanol (Slavus Ltd., Bratislava, SR) and benzene (Lachema n.e., Brno, CR) were UV spectroscopy grade. Chloroform, (Lachema n.e., Brno, CR) was analytical reagent grade. Tetrahydrofuran (BDH, London) was analytical reagent. Heptadecane (Fluka AG, Switzerland) was analytical reagent (dynamic viscosity η_{dyn} (20°C)=4.209 cP, activation energy of flow $E_a=15 \text{ kJ mol}^{-1}$). Polybutene oils of various viscosity as Hyvis 07 (η_{dyn} (20°C)=647 cP, $E_a=55 \text{ kJ mol}^{-1}$), Hyvis 3 (η_{dyn} (20°C)=5 875 cP, $E_a=63 \text{ kJ mol}^{-1}$) and Hyvis 10 (η_{dyn} (20°C)=41 232 cP, $E_a=71 \text{ kJ mol}^{-1}$) were from BP Chemicals Ltd., London, England. The polybutenes were used as received.

2.1. Benzyl (1-pyrenylmethyl) ether (II)

2.1.1. Benzyl (1-pyrenylmethyl) ether (II)

1-Pyrenylmethanol (I) (0.464 g (2 mmol)), 0.3 g (2.2 mmol) of benzylchloride and 0.064 g (0.2 mmol) of tetrabutylam-



R	
I. H	1PyCH ₂ OH
II. CH ₂ C ₆ H ₅	1PyCH ₂ OCH ₂ C ₆ H ₅
III. CH ₂ C ₁₆ H ₉	1PyCH ₂ OCH ₂ Py
IV. (CH ₂) ₄ C ₁₆ H ₉	1PyCH ₂ O(CH ₂) ₄ Py

Scheme 1.

monium bromide were added to a stirred mixture of 0.42 g (10.5 mmol) of NaOH pellets in 0.4 ml of distilled water at the ambient temperature. After 4 days stirring, no I was detected. The crude product was crystallized three times from 20 ml of methanol to yield 0.2 g (31%) of yellow needles, mp at 58–59°C.

¹H NMR (CDCl₃) δ : 4.67 (s, 2H, CH₂Ph), 5.26 (s, 2H, 1-Py-CH₂), 7.27–7.45 (m, 5H, phenyl), 7.97–8.40 (m, 9H, 1-Py).

2.1.2. Di(1-pyrenylmethyl) ether (III)

Chloromethyl-1-pyrene was prepared by stirring 2 mmol of I and 3 mmol of thionyl chloride in 1 ml of benzene at ambient temperature during 18 h under argon. With stirring at ambient temperature, 0.174 g (4.35 mmol) NaOH pellets, were gradually added to 0.18 ml water, 0.184 g (0.79 mmol) of I, 0.198 g (0.79 mmol) of chloromethyl-1-pyrene, 2 ml of benzene, and 0.034 g (0.105 mmol) of tetrabutylammonium bromide under argon. Stirring was continued under argon atmosphere in the dark for 1 week. The mixture was suspended in 50 ml of methanol and filtrated. The obtained solid was extracted with 30 ml of hot toluene and filtered, 0.27 g (71%) of product, mp 174.5–177.5°C, crystallized from the filtrate. ¹H NMR (CDCl₃) δ : 5.37 (s, 4H, CH₂), 8.01–8.40 (m, 18H, aromatic).

2.2. 4-(1-Pyrenyl)butyl (1-pyrenylmethyl) ether (IV)

4-(1-Pyrenyl)-1-butanol (0.3023 g (1.10 mmol)), 0.277 g (1.10 mmol) of chloromethyl-1-pyrene, 3 ml of benzene and 0.45 g (0.140 mmol) tetrabutylammonium bromide were added to a stirred mixture of 0.35 g (8.75 mmol) of NaOH pellets in 0.35 ml of distilled water at ambient temperature. Stirring was continued under argon in the dark for 52 h. The product was suspended in methanol and filtered. The crude solid was dissolved in boiling toluene with charcoal and filtrated through a small layer of silica gel. Product (0.284 g, 53%) of mp 158–160°C crystallized from the toluene.

¹H NMR (CDCl₃) δ : 1.73–2.00 (m, 4H, –O–CH₂–CH₂–CH₂–CH₂–), 3.22–3.33 (t, 2H, 1-Py–CH₂–), 3.62–3.73 (t, 2H, –O–CH₂–), 5.21 (s, 2H, 1-PyCH₂–O–), 7.72–8.40 (m, 18H, aromatic).

Polymer films doped with probes were prepared by casting from solution or by hot pressing of impregnated powders. The following films were used as matrices: polystyrene (PS, Krasten, Kaucuk Kralupy a.s., CR, SEC (chloroform) $M_n=93\ 700$, $M_w/M_n=2.7$, $M_w=1.1 \times 10^5$ light scattering), polymethyl methacrylate (PMMA, Považské Chemické Závody, a.s. Žilina, SR, $M_v=1.01 \times 10^5$), polyvinyl chloride (PVC, Neralit 628, Spolana Neratovice, a.s., ČR $M_v=1.11 \times 10^5$), atactic polypropylene (aPP, Slovnaft a.s., Bratislava, SR $M_v=9.3 \times 10^3$), low density polyethylene (LDPE, Bralen 2–19, MFI=1.7–2.3/10 min, $d=0.916\text{--}0.919 \text{ g cm}^{-3}$ Slovnaft a.s., SR), and ultra high molecular weight polyethylene (UHMW PE GUR 4120,

Ticona, F.R.G.). Films were prepared for all polymers except polyethylene by casting 0.02–2 mg of probe in 1 ml chloroform or tetrahydrofuran solution of polymer (5 g/100 ml) on a quartz or glass plate (28×35 mm). Polyethylene films were prepared by hot pressing of impregnated powder (160°C for 5 min).

UV/VIS absorption spectra were recorded on a model M-40 Zeiss spectrophotometer. Emission spectra were recorded on a Perkin–Elmer MPF-4 spectrofluorimeter, which was connected through an interface and an A/D converter to a microcomputer [10] for data collection, processing and plotting on an XY plotter. The excitation wavelength was in the range 335–350 nm. Emission of solutions was measured in 1 cm cuvettes using a right-angle arrangement. The quantum yields for emission were determined relative to anthracene in methanol [5,6]. Emission of polymer films was measured in a front-face arrangement using a Perkin Elmer solid sample holder. The relative quantum yield for emission of each probe in each polymer film, was determined using anthracene in the same polymer as standard. The viscous solutions and polymer films were checked for background emission, which was at least an order of magnitude lower in the most unfavorable case (low concentration of probe and high background emission).

The relative quantum yields in film were determined according to the relation [11],

$$\Phi_F = \Phi_F^S \frac{\int_0^\infty I_F(\nu) d\nu}{\int_0^\infty I_F^S(\nu) d\nu} \left(\frac{1 - 10^{-A^S}}{1 - 10^{-A}} \right) \quad (1)$$

where Φ_F^S is the quantum yield of anthracene as a standard which was assumed to be 0.25 for all environments. For relative quantum yield, the value of Φ_F^S for anthracene was put at 1. Integrals $\int_0^\infty I_F(\nu) d\nu$ and $\int_0^\infty I_F^S(\nu) d\nu$ are areas under the emission curve of the investigated compound and

standard, and A and A^S are absorbances of the investigated compound and standard, respectively.

Fluorescence lifetime measurements were performed on a LIF 200 (Lasertechnik Ltd., Berlin, F.R.G.) which operates as a stroboscope. The excitation source was a nitrogen laser ($\lambda=337$ nm) and emission was selected by cut-off filters. The output signal was digitized and transferred to a microcomputer [12]. Since the fluorescence lifetimes of pyrene and its derivatives are $>10\times$ the halfwidth of the nitrogen laser (0.5 ns), simple linear least-square fits of the data without deconvolution were applied to mono- and biexponential functions [13]. The standard deviation $G^{1/2} = \Sigma((I_{\text{exp}} - I_{\text{calc}})^2/n)^{1/2}$, where I_{exp} and I_{calc} are experimental and calculated intensities of emission, respectively, was used to judge the quality of fit. It was assumed that decays were monoexponential if $G^{1/2}$ is $<5\%$.

Static and time-resolved measurements were performed on deaerated solutions (argon bubbling for 10 min). All measurements on polymer films were done in the presence of air.

Relevant spectral data of pyrene and probes I–IV in various media are given in Tables 1–5.

3. Results and discussion

Absorption spectra of bichromophoric probes based on pyrene are nearly the same as monosubstituted derivatives of pyrene with simple alkyl substituents in the region of $S_2 \leftarrow S_0$ and higher transitions in solutions and polymer matrices (Fig. 1). The absorption spectra reveal no interaction between pyrenyl chromophores (e.g. in di(1-pyrenylmethyl)ether (III)). This probe exhibits the same absorption spectrum in solution and in a solid matrix (Fig. 2). A small bathochromic shift and small broadening

Table 1
Spectral properties of pyrene in various solvents and polymer matrices

M ^a	λ_{abs} (log ϵ) (nm) ^b	λ_{em} (I_r) (nm) ^c	Φ_r ^d	A^e	τ (nm) ^f	$G^{1/2g}$	r^h
Cy	334 (4.53)	386 (1.00) 395 (0.65)	1.95	109	414	2.1	0.9978
MeOH	332 (4.77)	374 (1.00) 395 (0.93)	0.79	108	285	1.6	0.9990
CHCl ₃	336 (4.66)	376 (1.00) 396 (0.74)	1.08	107	133	1.1	0.9993
PS	340 (4.40)	376 (0.86) 396 (1.00)	0.58	97	249	0.8	0.9996
PMMA	336 (4.78)	375 (1.00) 396 (0.99)	1.04	83	226	3.1	0.9968
PVC	339 (4.51)	376 (1.00) 396 (0.70)	0.98	77	166	3.9	0.9969
aPP		369 (0.34) 384 (1.00)	0.72	87	313	1.0	0.9994
LDPE		387 (1.00) 396 (0.83)	2.08	89	269	2.1	0.9979
UHPE	336 (4.78)	386 (1.00) 396 (0.74)	1.17	100	368	0.8	0.9995

^a Medium: Cy, cyclohexane; MeOH, methanol; HCl₃, chloroform; PS, polystyrene; PMMA, polymethyl methacrylate; PVC, polyvinylchloride; LDPE, low density polyethylene; UHPE, ultra high molecular weight polyethylene.

^b Absorption maximum of band which was excited (decadic logarithmus of extinction coefficient).

^c Maximum of emission band (Relative intensity).

^d Relative quantum yield to anthracene under the same conditions.

^e Calculated value of preexponential factor of monoexponential fitting. The experimental value is set to 100.

^f Lifetime.

^g Standard error.

^h Correlation coefficient of the dependence log I on t .

Table 2
Spectral properties of 1-pyrenemethanol (I) in various solvents and polymer matrices

M ^a	λ_{abs} (log ϵ) (nm) ^b	λ_{em} (I_r) (nm) ^c	Φ_r ^d	A^e	τ (nm) ^f	$G^{1/2g}$	r^h
Cy	340 (4.85)	389 (1.00) 396 (0.98)	1.09	115	275	3.2	0.9972
MeOH	339 (4.70)	378 (1.00) 396 (0.96)	0.31	107	151	2.2	0.9974
HCCl ₃	344 (4.64)	379 (1.00) 398 (0.64)	0.99	90	101	1.7	0.9993
aPP	342 (4.33)	390 (0.97) 396 (1.00)	0.67	88	200	2.8	0.9976
PS	346 (4.25)	379 (0.89) 398 (1.00)	0.85	92	176	1.9	0.9987
PMMA	344 (4.66)	377 (1.00) 397 (0.72)	0.45	84	149	3.4	0.9974
PVC	346 (4.42)	378 (1.00) 398 (0.65)	1.81	66	104	6.1	0.9894
LDPE	345 (4.02)	396 (1.00)	2.88	91	223	1.8	0.9965
UHPE	345 (4.74)	378 (0.59) 390 (1.00)	0.78	90	236	2.3	0.9978

^a Medium: Cy, cyclohexane; MeOH, methanol; HCCl₃, chloroform; PS, polystyrene; PMMA, polymethyl methacrylate; PVC, polyvinylchloride; LDPE, low density polyethylene; UHPE, ultra high molecular weight polyethylene.

^b Absorption maximum of band which was excited (decadic logarithmus of extinction coefficient).

^c Maximum of emission band (Relative intensity).

^d Relative quantum yield to anthracene under the same conditions.

^e Calculated value of preexponential factor of monoexponential fitting. The experimental value is set to 100.

^f Lifetime.

^g Standard error.

^h Correlation coefficient of the dependence log I on t .

of absorption bands are due to the interaction with the polar PVC matrix rather than to interactions between pyrene chromophores. The long wavelength $S_1 \leftarrow S_0$ transition, which is observed at 375 and 390 nm with log $\epsilon \div 2$ in solutions, appeared for probe II in several polymer matrices at 400 nm with log $\epsilon \div 3$. This transition was not observed for probes with bulkier groups (III and IV). Generally, the changes in absorption spectra of probes I–IV were small so that no conclusion concerning the character of polymer matrix is possible [14].

Emission spectra of probes derived from pyrene exhibit vibrationally resolved fluorescence in the region 375–420 nm, which corresponds to the monomeric species (Figs. 3 and 4). A broad red-shifted emission band was observed for bichromophoric probes III (Fig. 5) and partially for IV (Fig. 6) in the region 450–500 nm. In the monomeric region, the vibrational bands appear around 377–380, 385–390, 395–400, and 410–415 nm. The relative intensity of these bands depends on the medium. The clear correlation between polarity of the medium and the intensity of the vibra-

Table 3
Spectral properties of 1-pyrenemethylbenzylether (II) in various solvents and polymer matrices

M ^a	λ_{abs} (log ϵ) (nm) ^b	λ_{em} (I_r) (nm) ^c	Φ_r ^d	A^e	τ (nm) ^f	$G^{1/2g}$	r^h
Cy	342 (4.76)	388 (1.00) 396 (0.92)	1.21	110	324	2.4	0.9979
MeOH	339 (4.65)	377 (1.00) 396 (0.76)	0.44	113	257	2.8	0.9983
HCCl ₃	345 (4.67)	379 (1.00) 398 (0.86)	2.23	91	119	1.5	0.9991
aPP	344 (4.53)	389 (1.00)	0.93	73	193	4.5	0.9951
PS	347 (4.08)	378 (0.37) 391 (1.00)	0.51	91	9	1.2	
				9	173		
PMMA	344 (4.66)	377 (0.53) 389 (1.00)	0.61	92	10	1.1	
				8	174		
PVC	347 (4.35)	390 (1.00) 411 (0.27)	1.72	94	9	1.1	
				6	110		
LDPE	346 (4.58)	378 (0.46) 390 (1.00)	1.83	95	231	1.8	0.9988
UHPE	345 (4.81)	397 (1.00)	2.03	98	268	1.2	0.9993

^a Medium: Cy, cyclohexane; MeOH, methanol; HCCl₃, chloroform; PS, polystyrene; PMMA, polymethyl methacrylate; PVC, polyvinylchloride; LDPE, low density polyethylene; UHPE, ultra high molecular weight polyethylene.

^b Absorption maximum of band which was excited (decadic logarithmus of extinction coefficient).

^c Maximum of emission band (Relative intensity).

^d Relative quantum yield to anthracene under the same conditions.

^e Calculated value of preexponential factor for monoexponential fit. The experimental value was set to 100. Calculated values of preexponential factor in biexponential fit.

^f Lifetime.

^g Standard error.

^h Correlation coefficient of the dependence log I on t .

Table 4
Spectral properties of di(1-pyrenemethyl)ether (III) in various solvents and polymer matrices

M ^a	λ_{abs} (log ϵ) (nm) ^b	λ_{em} (I_r) (nm) ^c	Φ_r ^d	A^e	τ (nm) ^f	$G^{1/2g}$	r^h
Cy	345 (4.86)	388 (0.06) 493 (1.00)	1.12	106	56	0.5	0.9998
MeOH	341 (4.71)	377 (0.09) 496 (1.00)	0.49	105	55	1.9	0.9992
HCCl	348 (5.04)	397 (0.08) 498 (1.00)	2.22	106	49	1.0	0.9998
aPP	345 (4.41)	378 (1.00) 397 (0.51)	0.62	95	194	1.6	0.9993
PS	347 (4.45)	378 (0.90) 398 (1.00)	0.35	67	10	0.8	
				33	133		
PMMA	345 (4.45)	377 (1.00) 397 (0.83)	0.55	61	14	1.0	
				39	116		
PVC	346 (4.62)	378 (1.00) 398 (0.65)	0.61	80	10	1.1	
				20	107		
LDPE	348 (4.78)	389 (1.00) 398 (0.54)	1.51	95	225	1.5	0.9987
UHPE	347 (5.11)	390 (1.00)	1.22	87	235	3.45	0.9952

^a Medium: Cy, cyclohexane; MeOH, methanol; HCCl₃, chloroform; PS, polystyrene; PMMA, polymethyl methacrylate; PVC, polyvinylchloride; LDPE, low density polyethylene; UHPE, ultra high molecular weight polyethylene.

^b Absorption maximum of band which was excited (decadic logarithmus of extinction coefficient).

^c Maximum of emission band (Relative intensity).

^d Relative quantum yield to anthracene under the same conditions.

^e Calculated value of preexponential factor of monoexponential fitting. The experimental value is set to 100. Calculated values of preexponential factor in biexponential fit.

^f Lifetime.

^g Standard error.

^h Correlation coefficient of the dependence log I on t .

tional bands has not been yet established for probes I–IV (as it has for unsubstituted pyrene [15,16]). Usually, for probe I, the most intense bands are at 386 and 396 nm in non-polar matrices. The band at 377 nm is less intense. On the other hand, the band at 377 nm is the more intense in polar matrix like PVC (Fig. 3). The vibrational band at 377 nm for probe II is weak in all matrices (Fig. 4). The emission spectrum is dominated by the band at 386 nm. Bichromophoric probe III gives exclusively excimer emission (Fig. 5) in solvents like cyclohexane, methanol and dichloromethane.

By contrast, monomeric emission is exclusively observed from probe III in glassy polymer matrices below T_g (PS, PMMA, PVC), in a rubbery, amorphous matrix (aPP), and in a semi-crystalline matrix (PE). Strong vibrational bands are observed at 377 and 396 nm in non-polar aPP as well as in more polar PVC (Table 4). The unsymmetrical bichromophoric probe IV exhibits a weak band in the excimer region at 449 nm in liquid solvents and no band in this region in polymer matrices (Fig. 6). The vibrational band at 377 nm is the most intense in the emission spectrum of

Table 5
Spectral properties of 1-pyrenemethyl-4-(1-pyrene)butylether (IV) in various solvents and polymer matrices

M ^a	λ_{abs} (log ϵ) (nm) ^b	λ_{em} (I_r) (nm) ^c	Φ_r ^d	A^e	τ (nm) ^f	$G^{1/2g}$	r^h
Cy	342 (4.95)	378 (1.00) 398 (0.56) 420 (0.18) 449 (0.17)	2.34	103	142	0.6	0.9999
MeOH	342	378 (1.00) 397 (0.48) 439 (0.10) 448 (0.10)	1.16	101	133	0.8	0.9996
HCCl ₃	345 (4.88)	378 (1.00) 399 (0.37)	0.75	106	72	0.7	0.9991
PS	346 (4.63)	379 (1.00) 399 (0.40)	0.29	90	162	2.1	0.9988
PMMA	344 (4.65)	378 (1.00) 398 (0.39)	0.72	80	155	3.8	0.9976
PVC	346 (5.13)	380 (1.00) 399 (0.82)	1.04	79	116	4.4	0.9947
LDPE	345 (4.62)	378 (1.00) 398 (0.54)	0.82	94	226	1.8	0.9987
UHPE	346 (4.96)	379 (1.00) 399 (0.82)	0.95	93	204	2.9	0.9974

^a Medium: Cy, cyclohexane; MeOH, methanol; HCCl₃, chloroform; PS, polystyrene; PMMA, polymethyl methacrylate; PVC, polyvinylchloride; LDPE, low density polyethylene; UHPE, ultra high molecular weight polyethylene.

^b Absorption maximum of band which was excited (decadic logarithmus of extinction coefficient).

^c Maximum of emission band (Relative intensity).

^d Relative quantum yield to anthracene under the same conditions.

^e Calculated value of preexponential factor of monoexponential fitting. The experimental value is set to 100.

^f Lifetime.

^g Standard error.

^h Correlation coefficient of the dependence log I on t .

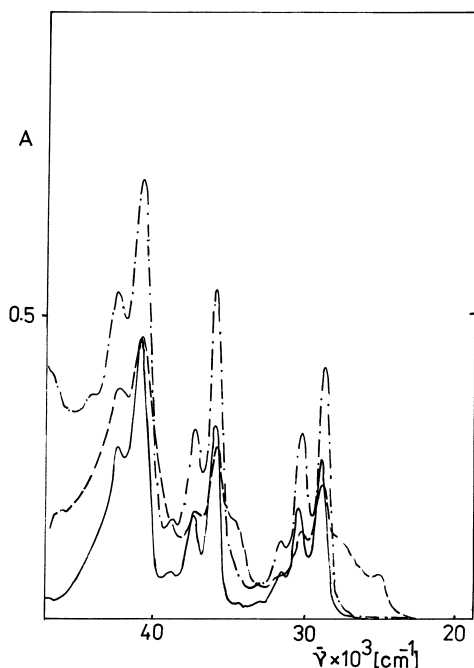


Fig. 1. Absorption spectra of probes I–III in PVC matrix at concentration $0.002 \text{ mol kg}^{-1}$ for I (—), II (-----), and III (-·-·-·-).

probe IV, as in the case of 1-pyrenebutyric acid derivatives [5]. Vibrational structure of the probes under study is more or less similar in glassy matrices prepared by casting or in semi-crystalline matrices prepared by hot pressing.

Relative fluorescence quantum yields Φ_r (relative to anthracene) lie in the range 0.5 to 2 in various solvents and polymer matrices. Anthracene was chosen as the standard its quantum yield should not be very dependent on the medium. The scatter of Φ_r for probes I–IV is considerable in solvents

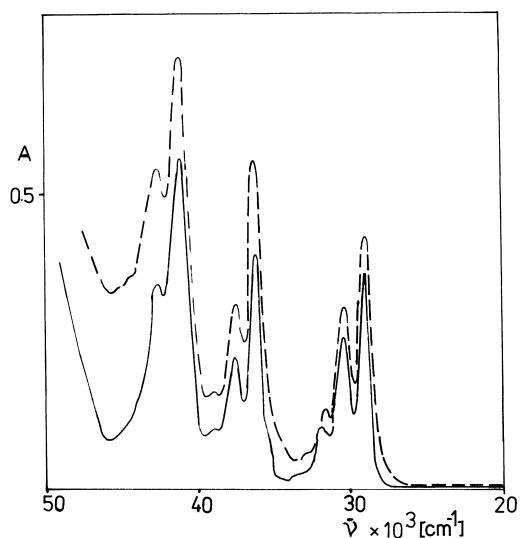


Fig. 2. Absorption spectrum of probe III at concentration $10^{-5} \text{ mol dm}^{-3}$ in cyclohexane (—) and at concentration $0.002 \text{ mol kg}^{-1}$ in PVC (-----).

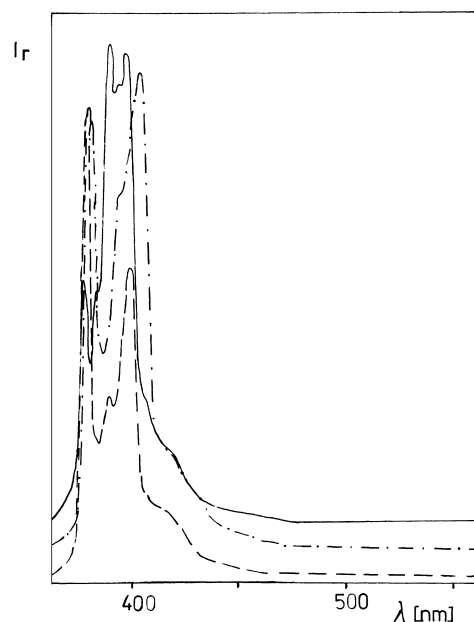


Fig. 3. Emission spectrum of probe I in cyclohexane at concentration $10^{-5} \text{ mol dm}^{-3}$ (— in offset), in polymer matrices PS (----- in offset), and PVC (-·-·-·-) at concentration $0.002 \text{ mol kg}^{-1}$.

and even more so in polymer matrices. This scatter may indicate that the assumption concerning anthracene may not be strictly fulfilled. These data do not show any trend with respect to the value of the medium. On the other hand, no large increase or decrease in Φ_r is noticeable. In chlorinated solvents, Φ_r for probes II and III seem to be rather

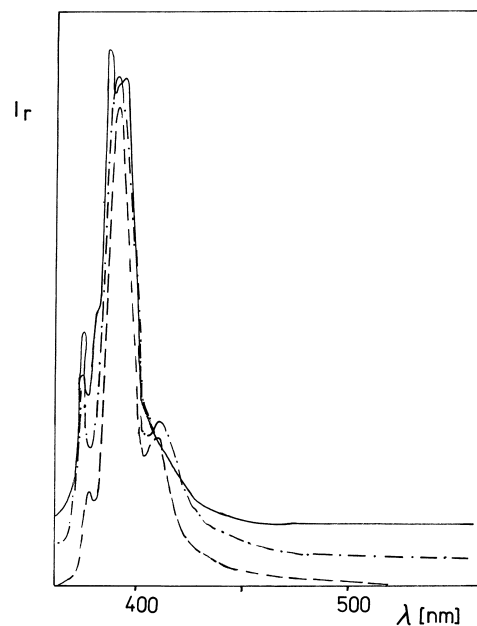


Fig. 4. Emission spectrum of probe II in cyclohexane at concentration $10^{-5} \text{ mol dm}^{-3}$ (— in offset), in polymer matrices PS (----- in offset), and PVC (-·-·-·-) at concentration $0.002 \text{ mol kg}^{-1}$.

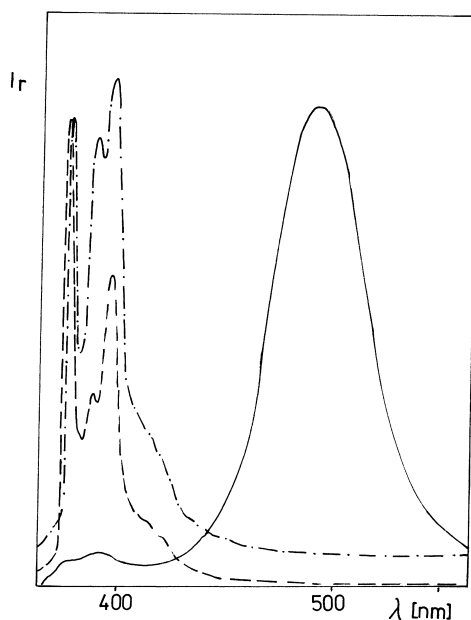


Fig. 5. Emission spectrum of probe III in cyclohexane at concentration $10^{-5} \text{ mol dm}^{-3}$ (—), in polymer matrices PS (..... in offset) and PVC (-----) at concentration $0.002 \text{ mol kg}^{-1}$.

high. In any case, it can be concluded that the medium does not exhibit a strong quenching effect on the probes.

Time-resolved measurements provide additional information on the influence of the medium on spectral properties. The decay of fluorescence emission in the monomeric region of pyrene and probe I is monoexponential in the solvents and in the polymer matrices (Fig. 7). The longest lifetime,

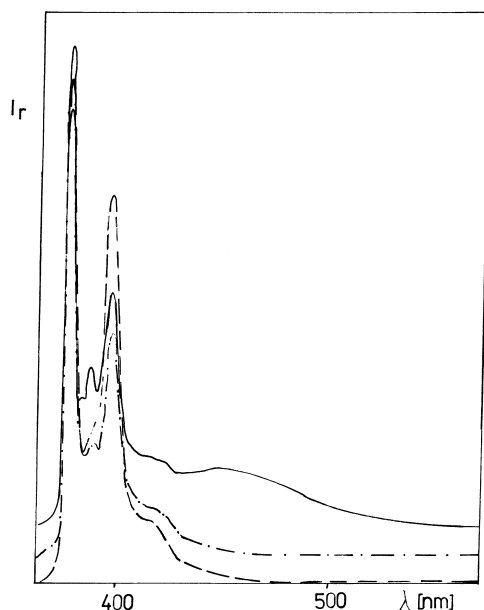


Fig. 6. Emission spectrum of probe IV in cyclohexane at concentration $10^{-5} \text{ mol dm}^{-3}$ (— in offset), in polymer matrices PS (..... in offset) and PVC (-----) at concentration $0.002 \text{ mol kg}^{-1}$.

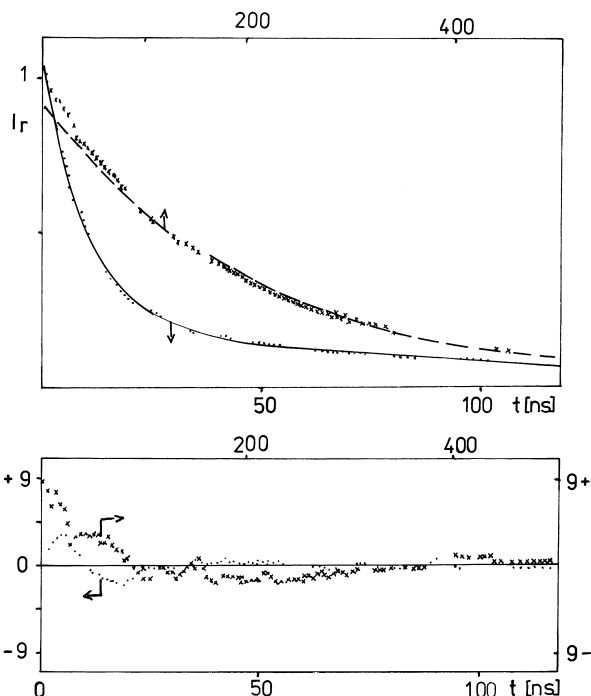


Fig. 7. Decay curve of monomer fluorescence of probe III at concentration $0.002 \text{ mol kg}^{-1}$ in LDPE (.....) and PVC (—). Monomer fluorescence decay of III in LDPE is fitted to monoexponential function (broken line) and decay of III in PVC is fitted to biexponential function (full line).

414 ns, is exhibited by pyrene in deaerated cyclohexane (Table 1). Lifetimes of pyrene in more polar solvents are shorter. The lifetimes of probe I are shorter than the lifetime of pyrene in all solvents and polymer matrices (Tables 1 and 2). The standard error for fitting the decay of pyrene and probe I to a monoexponential function is about 1–2% in the solvents and 2–4% in polymer matrices. The experimental value of the preexponential factor A_0 was set at 100. Deviation of the calculated A_0 from 100 indicates the quality of the fitting. In more polar matrices, the deviation of A_0 and the standard error for decay increase more for probe I than for pyrene. The decay of the curve of 10^{-4} mol/dm^3 pyrene in most solvents exhibited a slight increase at the beginning. Consequently, the preexponential factor A_0 was larger than 100 when the whole curve was fit to a monoexponential function. Similarly to pyrene, the longest lifetime of probe II was observed in cyclohexane. In non-polar aPP, the decay of II can be fitted to a monoexponential, but the standard error is ca 5%. In matrices such as PS, PMMA and PVC, the decay is clearly biexponential. Besides a long ($\tau > 100 \text{ ns}$), a shorter emission with $\tau \sim 10 \text{ ns}$ appears. Such a short lived emission was also observed in polar medium, the sodium salt of polyacrylic acid [6]. This short lived emission was explained as a consequence of a strong ionic field. This explanation cannot be easily applied to the short lived emission of probe II in polymer matrices, although the polarity of a polymer matrix as well as conformational effects may play some role. Bichromophoric probe III exhibits

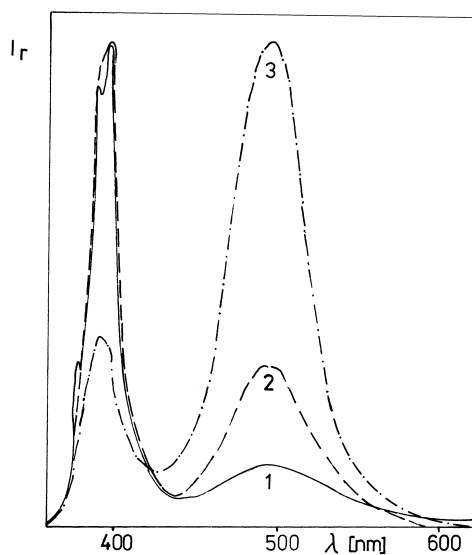


Fig. 8. Influence of temperature on emission spectra of probe III ($c=10^{-5}$ mol dm $^{-3}$) in mixture Hyvis 07/cyclohexane (9:1) at temperature 10°C (—), 20°C (-----) and 40°C (-·-·-·-).

very weak monomer emission and intense excimer emission with τ in the range of 40–60 ns in non-polar as well as polar solvents. The decay of this emission in solutions obeys a monoexponential function with an excellent correlation coefficient (>0.999) (Table 4) and A_0 slightly higher than 100. In non-polar matrices such as aPP, LDPE and UHPE, the only monomer emission observed is that which decays with a lifetime longer than 200 ns. A_0 is lower than 100. In more polar matrices as PVC, including polystyrene, the decay of emission is biexponential (Fig. 7). The fraction of short lived emission ($\tau \sim 10$ ns) is about 60–80%. The

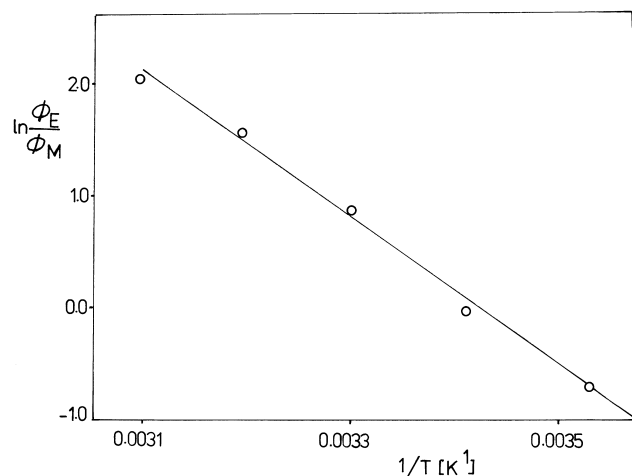


Fig. 9. Arrhenius plot of dependence of $\ln(\Phi_e/\Phi_m)$ on $1/T$ for probe III in mixture Hyvis 07/cyclohexane.

long lived emission has τ longer than 100 ns. The unsymmetrical probe IV exhibits emission whose decay fits a monoexponential function, although its emission includes some excimer. The monomeric emission has $\tau=220$ ns in non-polar LDPE. In the chlorinated solvent, HCCl $_3$, it is only 72 ns, and no long wavelength tail is observed in the emission spectrum. In polar PVC, the lifetime is 116 ns.

Pyrene, probe I in all matrices, and probe II, in non-polar matrices exhibit decays which can be fitted to monoexponential functions. In all solid matrices, two effects are observed. When fitted to monoexponential functions A_0 is lower than 100 and the decay at early times is faster, as fits to monoexponential function. This part of the decay curve represents the smaller part of the curve, and its analysis is

Table 6
Decay of emission of probe III in different solvents at various temperatures

Solvent	η_{dyn} (20°C) (cP) ^a	Temperature (°C)	A^b	τ (ns) ^c ns	$G^{1/2d}$	r^e	E'_a (kJ mol $^{-1}$) ^f	E''_a (kJ mol $^{-1}$) ^g
Benzene	0.6	8	106	48	1.0	0.9995		
		60	96	40	2.5	0.9991		
C $_{17}$ H $_{36}$	4.2	20	79	10	0.8		39.6	22.8
		50	21	129	4.5	0.9991		
Hyvis07	647.0	10	82	69	0.7		75.0	54.0
		20	69	6				
Hyvis 3	5875.0	20	31	129				
		50	85	8	1.3			
Hyvis 10	41232.0	20	15	111				
		50	93	52	1.4	0.9992		
		60	70	9	1.8		87	
		60	30	82				
		60	105	77	2.9	0.9939		

^a Dynamic viscosity at 20°C.

^b Calculated value of preexponential factor. Experimental value was set to 100.

^c Lifetime.

^d Standard error.

^e Correlation coefficient of the dependence $\log I$ on t .

^f Activation energy calculated from dependence $\ln(\phi_0/\phi)$ on $1/T$.

^g Activation energy calculated from dependence $\ln(\phi_e/\phi_m)$ on $1/T$.

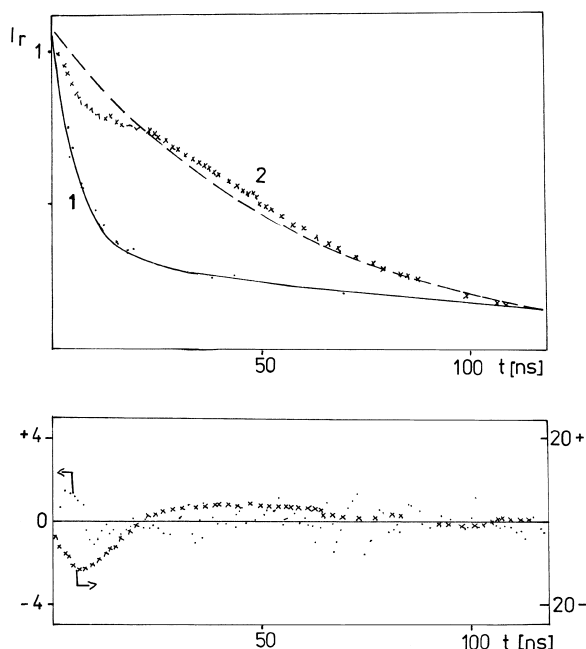


Fig. 10. Decay curve of emission probe III ($c=10^{-5}$ mol dm $^{-3}$) in mixture Hyvis 07/cyclohexane (9:1) at temperature 10°C (—) and 40°C (-----). The decay curve at 10°C was fitted to biexponential function and decay at 40°C was fitted to monoexponential function.

less precise since the number of experimental points is limited. In most cases, it was possible to fit the decay curve of pyrene and probe I doped in polymer matrices to biexponential functions, although fitting to monoexponential functions was quite satisfactory. The shorter lifetime lies in the range 40–100 ns. It indicates that there is some aggregation of pyrene and probe I even at low concentrations (10^{-3} mol kg $^{-1}$) in non-polar matrices. This aggregation is not noticeable in the excimer region in static emission spectra, but it appears in the kinetics of the decay.

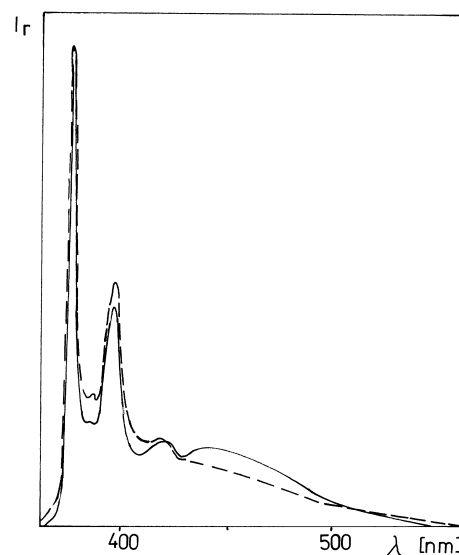


Fig. 11. Emission spectrum of probe IV in methanol ($c=10^{-5}$ mol dm $^{-3}$) at temperature 20°C (—) and 50°C (-----).

Three regions of lifetimes, obtained upon analyses of decay curves under different conditions, are >100 ns, ~50 ns and ~10 ns. The longest lifetime belongs the monomeric emission. Typical excimer emission is observed in solutions of probe III. For other probes doped in polymer matrices, the lifetime in the region 40–100 ns indicates ground state aggregation. These aggregates emit excimer-like emission, which decays faster than monomeric emission. The origin of the emission with a lifetime around 10 ns is not completely clear.

Since no excimer emission of probe III was observed in polymer matrices, and the decay in several matrices was clearly biexponential (Fig. 7), the possible formation of

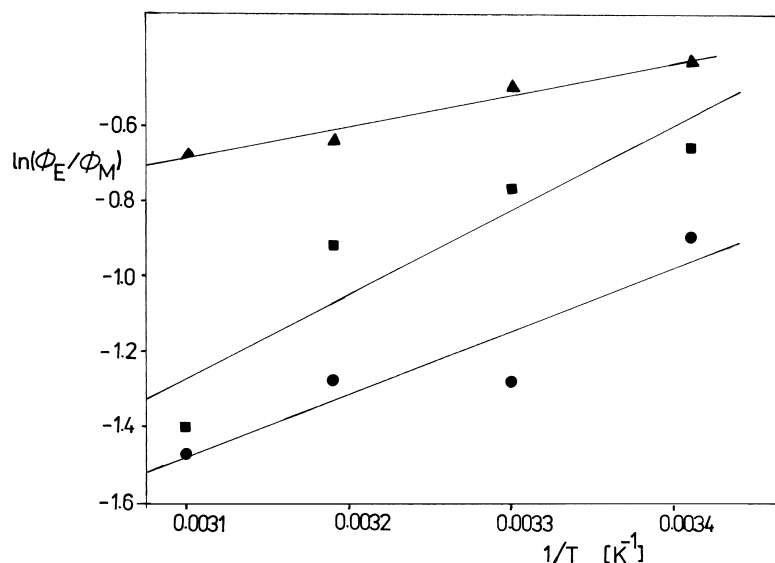


Fig. 12. Arrhenius dependence for probe IV of $\ln(\Phi_E/\Phi_M)$ on $1/T$ in cyclohexane (■), dichloromethane (●) and methanol (▲).

intramolecular excimers was examined in highly viscous liquids. Their microstructure is between that of polymer films and low viscosity solvents. Clearly, the intensity of excimer emission of probe III increases in polybutene oil Hyvis 07 in the temperature range 10–40°C (Fig. 8). This change can be expressed as a ratio of relative quantum yield of monomeric emission at lower and higher temperature Φ_0/Φ or as a ratio of quantum yields of excimer to monomer emission Φ_e/Φ_m . In either case the slope of a plot $\ln(\Phi_0/\Phi)$ or $\ln(\Phi_e/\Phi_m)$ versus $1/T$ can be ascribed to an activation energy (E_a). In the former case, E'_a is an activation energy for singlet deactivation processes including the formation of excimer. In the latter case, E''_a is an activation energy for excimer formation (Fig. 9). In both cases, the value of E'_a and E''_a increases with viscosity of the medium, but not proportionally. From heptadecane to Hyvis 07 the dynamic viscosity changes about 100 times, but the value of E'_a and E''_a increases two fold (Table 6). An increase of viscosity represents a hindrance to deactivation of the singlet state through formation of an excimer or another process related to rotation of a substituent. The increase of macroviscosity from heptadecane to Hyvis 10 is about 10^4 but the change in microviscosity is less dramatic. However, when both macro- and microviscosity in the solid polymer are substantial, no conformational change can take place, and no excimer emission is observed. Monomer and excimer emission of probe III is observed in the limited viscosity range of viscous liquids where the ratio of excimer to monomer emission can be used to monitor this parameter. The dependence of the lifetime of excimer emission from probe III on temperature in benzene solution is small (Table 6). The decay in the temperature range 7.5–60°C is monoexponential. On the other hand, the decay of monomeric emission of probe III in viscous Hyvis 07 requires a biexponential fit (Fig. 10) with a shorter lifetime ~ 10 ns and with a longer lifetime >100 ns. These lifetimes were observed for probe III in some polymer matrices. With increasing temperature the decay of emission becomes monoexponential. This clearly shows that the short lived emission originates from a 'frozen conformation', which is formed at the casting stage of polymer films or at a low temperature in viscous solvents. Increased temperature leads to relaxation of this conformation.

Bichromophoric probe IV exhibits an emission spectrum with a band at 450 nm in methanol and cyclohexane, but it is very weak in dichloromethane. With increasing temperature, the intensity of this band decreases (Fig. 11). Attaining

a conformation suitable for excimer formation is less favorable for probe IV than for probe III. With increasing temperature, the dissociation of excimer prevails over its formation. Therefore, a plot of $\ln(\Phi_e/\Phi_m)$ versus $1/T$ (Fig. 12) gives the activation energy of the excimer decomposition, E'''_a which is low in methanol (6.9 mol kg⁻¹) and rather high in cyclohexane (18.6 mol kg⁻¹). Clearly, the formation of intramolecular excimers in probe IV is not as effective as in probe III. It is also more sensitive to temperature.

In conclusion, the bichromophoric probes based on pyrene exhibit monomer emission in polymer matrices which decay in a complex manner.

Acknowledgements

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