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SPECTRAL CHARACTERISTICS OF FREE AND LINKED PYRENE-TYPE CHROMOPHORES IN SOLUTION, POLYMER MATRICES, AND INTERPENETRATING NETWORKS

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ABSTRACT

Monomers, 1-pyrenylmethyl methacrylate (PyMMA), 1-pyrenylbutyl methacrylate (PyBMA), 4-(1-pyrenyl)methoxymethyl styrene (PyMMS) and allyl-(1-pyrenylmehtyl) ether (PyMAE), with pyrene as chromophore, were prepared. Their spectral properties (absorption, emission and emission decay) in solution, and doped or bonded in polymer matrices and complex polymer systems as interpenetrating polymer networks (IPN), were investigated. Spectral properties of pyrene-containing monomers doped in polystyrene (PS), polymethylmethacrylate (PMMA), polyvinylchloride (PVC), polyethylene (PE) and grafted on PE as well as copolymerized in buthylmethacrylate-co-styrene copolymer (BMA-co-S) have been compared. Absorption and emission spectra of pyrene type probes in solution and in IPN matrices exhibit typical absorption of the pyrene moiety. For IPN with grafted probes on PE, the absorption is slightly shifted to red wavelength. For monomers, PyMMA, PyBMA and PyMAE grafted to PE, the shape of the emission spectrum depends on the wavelength of excitation. The ratio of intensity of the vibrational band, I_1/I_3, (I_1 peak at 377 nm and I_3 peak at 388 nm) has been a quite useful indicator of polarity of IPN. The relative quantum yields of fluorescence in IPN matrices are lower in comparison to polymer matrices of PE, PS, PMMA for all probes under study. The fluorescence life-times for bound and free probes have been in the range 100–200 ns, which is substiantialy shorter than for the parent pyrene chromophore under the same or similar condition.

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Grafted probes on PE alone, or as a part of IPN, exhibit substantially shorter life-time around 10 ns and decay is rather complex.

Key Words: Fluorescence technik; Pyrene; Monomers; Spectral characteristics, Polymer matrices; Interpenetrating polymers networks (IPNs).

INTRODUCTION

Fluorescence probes of various structure can be used to monitor photophysical and photochemical processes in different environments. The ultimate goal of these studies is to employ them for construction of various sensors [1]. Preferably, those parameters, which exhibit strong dependence on medium, are exploited in sensor technology. The application of fluorescence has several advantages due to its high sensitivity, simple detection and pronounced influence of the environment on suitable selected chromophores. Pyrene and its derivatives are widely used probes for study of different environments, including polymer micro-environments [2]. Perhaps the most important characteristic of pyrene utilized for study of polymer microenvironment is the strong dependence of its fluorescence emission vibronic structure and decay on the polarity of environment [3, 4]. The ratio of the first and the third peak in pyrene vibronic emission (I_1/I_3) is dependent upon the polarity of environment and has been used for the characterization of the polarity of various methacrylate-type polymers [5]. The change of pyrene vibronic structure (I_1/I_3 ratio) and fluorescence lifetime as a reporter of the polarity of microdomains have been successfully applied also for the study of phase-separated systems composed of organic polymers. These would include polymer blends and block copolymers. Characterization of polystyrene-poly(2-vinylpyridine) (PS-PVP) copolymer using pyrene and its derivatives as fluorescence probes indicated, that PS and PVP chains are not randomly mixed, but are phase separated [6].

The fluorescence experiments involving micro-heterogeneous media can be divided into two classes: those involving fluorescent labels, i.e., the fluorophore covalently bonded to one of the components; and those involving fluorescent probes, i.e., the fluorophore doped freely into the polymer [6].

The syntheses, thermal properties, and dynamic-mechanical behavior of interpenetrating polymer networks (IPN) [7, 8] consisting of polyethylene (PE) and poly(butyl methacrylate-co-styrene) (BMA-co-S) have been reported previously [9, 10]. This IPN system having a molar composition of structural unity (1:1 low density PE:7:3 BMA-co-S), shows transparent properties at room temperature. Here, we use it as support for spectral characterization of fluorescence probes and labels based on pyrene through the use of absorption and static and dynamic fluorescence measurements.

In this article, we describe the preparation and spectral characterization of new fluorescence probes in solution and in polymer matrices. Pyrenyl groups have been linked covalently to the PE part of the IPN by a grafting technique [11] and to the (BMA-co-S) copolymer part by terpolymerization of BMA, S and 1-

pyrenylmethyl methacrylate (PyMMA), 1-pyrenylbutyl methacrylate (PyBMA), 4-(1-pyrenyl)methoxymethyl styrene (PyMMS) or allyl (1-pyrenemethyl) ether (PyMAE). For comparison, spectral properties of pyrene-type monomers have freely been added to PE, grafted on PE and terpolymerized in BMA-co-S have been investigated. Polymers such as PE, polystyrene (PS), poly (methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC) doped with freely added pyrene and 1-pyrenylmethanol have been studied as well.

EXPERIMENTAL

The structures of the fluorescent probes used in this paper are shown in Scheme 1. The synthesis of the derivatives PyMMA and PyBMA were performed by re-esterification reaction of methyl methacrylate with the subsequent alcohol using tetrabutylorthotitanate (TBOT) as reesterification catalyst and with modification of some described procedures [12]. The derivatives PyMMS and PyMAE were prepared from 1-pyrenylmethanol and subsequent chloro derivative under conditions for phase-transfer reaction [13].

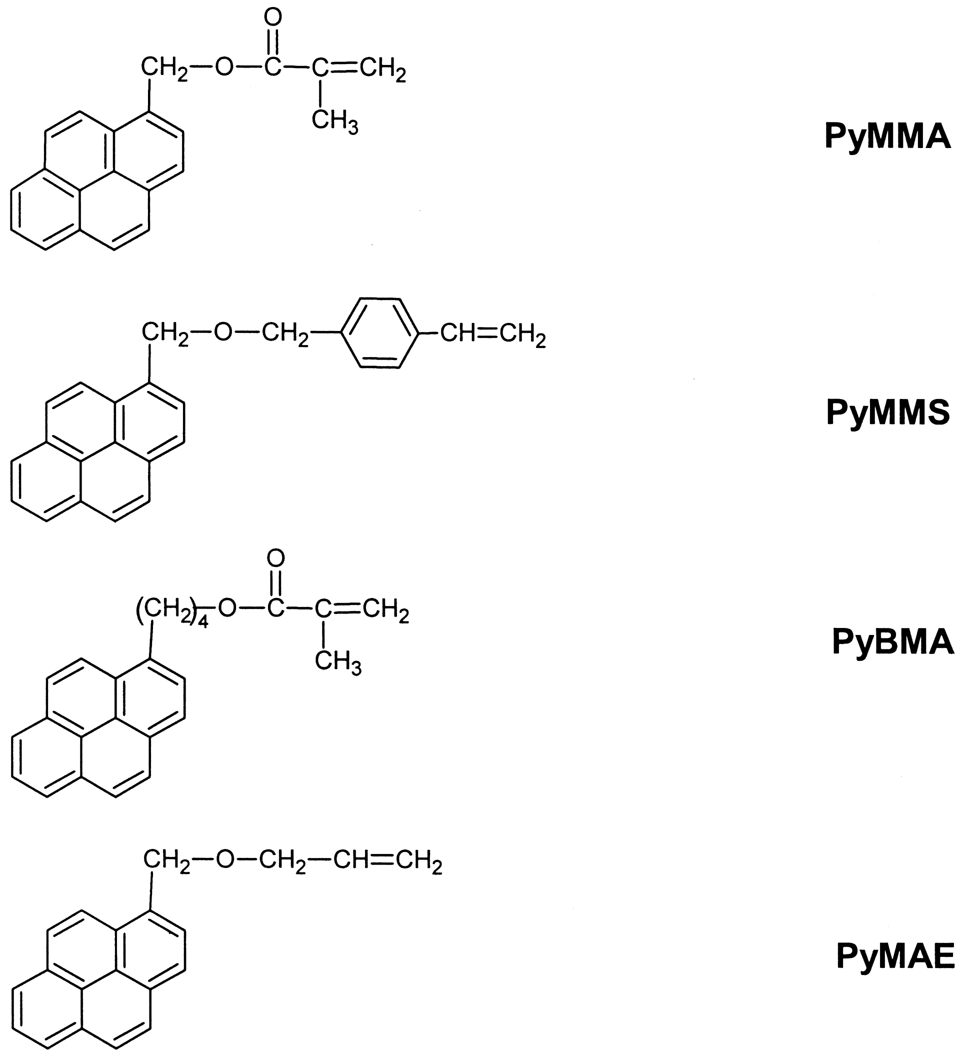
Preparation of Probes

1-Pyrenylmethyl Methacrylate (PyMMA). (I)

To a refluxing solution of 1-pyrenylmethanol (1 g, 4.3 mmol) (Aldrich, Steinheim, Germany, 98%) and polymerization inhibitor IONOL AO4K (0.012 g) in 30 ml of freshly distilled methyl methacrylate (MMA) were added three drops of tetrabutylorthotitanate (TBOT) as reesterification catalyst. The reaction was carried out under argon atmosphere for 4.5 hours. A small amount of polymeric PMMA, precipitated on cooling with the addition of 300 ml of methanol. After filtration, the solvent was removed under reduce pressure. The product was obtained by crystallization (3x) from methanol (0.3235 g, 25% of pale yellow crystals, m.p. 99.5–101.5°C). Elem. Anal.: Cald. (C) 83.98%, (H) 5.37%, Found (C) 84.27%, (H) 5.16%. ^{1}H NMR ($CDCl_3$) δ: 1.96–1.97 (m, 3H, CH_3), 5.56–5.57 (m, 1H, = CH_2 *cis*), 5.91 (s, 2H, CH_2-O), 6.14–6.15 (m, 1H, = CH_2 *trans*), 8.0–8.33 (m, 9H, pyrene). FTIR (KBr): ν(C = O) 1710 cm^{-1}, ν(C-O-C) 1168 cm^{-1}, ν(Pyr.) 845 cm^{-1}. MASS: 300.3 (M$^+$), 231.3, 215.2, 201, 69.1.

1-Pyrenylbutyl Methacrylate (PyBMA). (II)

1-Pyrenylbutanol (0.5 g, 1.82 mmol) (Aldrich, Steinheim, Germany, 98%) was refluxed in MMA as describe above with (I). The product was obtained by crystallization (2x) from ligroin (0.5 g, 80% of pale yellow crystals m.p. 75–77°C). ^{1}H NMR ($CDCl_3$) δ: 1.84–1.99 (m, 4H, -CH_2-CH_2-), 1.93–1.94



Scheme 1.

(m, 3H, CH_3), 3.36–3.41 (t, 2H, -CH_2-Arom.), 4.21–4.25 (t, 2H, -CH_2-O), 5.52–5.54 (m, 1H, = CH_2 *cis*), 6.09–6.1 (m, 1H, = CH_2 *trans*), 7.85–8.27 (m, 9H, pyr.). FTIR (KBr): ν(C = O) 1724 cm^{-1}, ν(pyr.) 841 cm^{-1}.

4-(1-Pyrenyl)methoxymethyl Styrene (PyMMS). (III)

To the magnetically stirred solution of 0.44 g (1 mmol) NaOH in 0.4 ml distilled water at room temperature, 1-pyrenylmethanol (0.464 g, 2 mmol), 1-(chloromethyl)-4-vinyl benzene, (0.305 g, 2 mmol) (Aldrich, Steinheim, Germany, 90%)

and of tetrabutylammonium bromide (0.064 g, 0.2 mmol) were added dropwise. The heterogeneous reaction mixture was stirred for 15 hours under argon atmosphere and then dissolved in methanol (75 ml). After removal of half the amount of solvent under reduced pressure, the crystals precipitated. Recrystallization from 60 ml of methanol yielded 0.46 g (66%) of white crystals (m.p. 74–75°C). ^{1}H NMR ($CDCl_3$) δ: 4.61 (s, 2H, -O-CH_2-), 5.22 (s, 2H, Py-CH_2-O), 5.21–5.25 (d, 1H, = CH_2, *cis*), 5.71–5.78(d, 1H, = CH_2, *trans*) 6.67–6.77 (dd, 1H, = CH), 7.33–7.41(dd, 4H, phenyl), 7.95–8.36 (m, 9H, pyr.). FTIR (KBr): ν(phen) 1628 cm^{-1}, ν(R-CH = CH_2) 1084 cm^{-1}, ν(pyr.) 845 cm^{-1}.

Allyl (1-pyrenylmethyl) ether (PyMAE). (IV)

To the magnetically stirred suspension of 0.465 g (2 mmol) of 1-pyrenylmethanol, 0.42 g (10 mmol) of NaOH and 0.5 ml distilled water at room temperature, allylchloride (0.306 g, 4 mmol) (Fluka AG, Germany, 98%) and tetrabutylammonium bromide (0.064 g, 0.2 mmol) were added dropwise as described in (III). The reaction mixture was stirred for 23 hours and then dissolved in ether. The ether solution was washed with water, dried over Na_2SO_4, and the solvent was removed under reduced pressure to leave an oily residue, which was separated on a silica gel column (120 g) by elution with a mixture of ligroin: ethyl acetate (20:1). The yield of green oily product was 0.44 g (80%). ^{1}H NMR ($CDCl_3$) δ: 4.19 (d, 2H, CH_2-CH), 5.25 (s, 2H, CH_2-O), 5.25–5.42 (dd, 2H, = CH_2), 6.07 (m, 1H, -CH =), 8.0–8.41 (m, 9H, pyr.). FTIR (neat): ν(R-CH = CH_2) 1078 cm^{-1}, ν(pyr.) 845 cm^{-1}.

Materials

Anthracene and pyrene (Lachema n.e., Brno, CR) were zonally refined. Solvents, cyclohexane (Merck, Darmstadt, Germany) and methanol (Slavus, Bratislava, Slovakia) were used for UV spectroscopy. Chloroform, dichloromethane and tetrahydrofuran (THF) (Lachema n.e., Brno, CR) were analytical grade reagent.

The inhibitor of polymerization was removed from butyl methacrylate (Merck, Schuchardt, Germany, 99%) and styrene (Chemapol, Prague, CR) before use by washing with aqueous sodium hydroxide (5 wt%) and water. After drying with Na_2SO_4, the monomers were distilled under reduced pressure. The crosslinker, 1,4-butanediol dimethacrylate (BDDM) (Aldrich, Steinheim, Germany, 95%) was used for crosslinking in IPN preparation. As initiator for IPN formation, 2,5-dimethyl-2,5-di-(tert-butylperoxy) hexane (Luperox 101) (Luperox, GmbH Germany) was used. For PE grafting, tert-butylperoxy-2-ethylhexanoate (TBPEH) (AKZO Chemie GmbH, Germany) or dibenzoylperoxide (BP) (Merck, Schuchardt, Germany, 75%) was used.

IPN networks were prepared by dissolving of PE and fluorescent probe (concentration of probes were 10^{-4} and 10^{-3} mol kg^{-1} on IPN) in monomers BMA and

S with molar ratio 7:3 at 110°C. The PE/monomers molar structural ratio was kept equal to 1. A small amount of inhibitor of polymerization (benzoquinone) was also used to prevent thermal polymerisation while dissolving PE in monomers. For all samples, 2 wt% Luperox 101 as initiator of polymerization and 1 mol% BDDM as cross-linking agent, were added. The resulting solution was poured between two glass plates, sealed on three sides by a silicon rubber tubing and put in the oven. The reaction was carried out at 110°C for 5 hours, followed by 1 hour at 160°C. The IPN with grafted PE and terpolymer S-co-BMA-co-Probe were prepared in the same way.

Polymer films doped with probes were prepared by casting from solution or by hot pressing of impregnated powders. The following polymers were used as matrices: polystyrene (PS, Krasten, Kaucuk Kralupy a.s., CR, SEC (chloroform) M_n = 93 700 M_w/M_n = 2.7), polymethyl methacrylate (PMMA, Povazské Chemické Závody, a.s. Zilina, SR, $M_v = 1.01 \times 10^5$), polyvinyl chloride (PVC, Neralit 628, Spolana Neratovice, a.s., CR $M_v = 1.11 \times 10^5$), atactic polypropylene (aPP, Slovnaft a.s., Bratislava, SR $M_v = 9.3 \times 10^3$), and low density polyethylene (LDPE, Bralen 2–19, MFI = 1.7–2.3 g/10 min, d = 0.916–0.919 g cm^{-3}, Slovnaft a.s., SR). Films were prepared for all polymers, except polyethylene, by casting on a glass plate (28 × 35 mm) a solution of polymer (5 g/100 ml) in 1 ml chloroform or tetrahydrofurane, containing a weighed amount of probe. The final concentration of probe was 0.002 mol kg^{-1}. PE powder, probe and 5 ml of dichloromethane were stirred for 24 hours for impregnation. PE films were prepared by hot pressing of impregnated powder (160°C for 1 minute). The thickness of films was 0.08–0.12 mm and content of probes ranget between 10^{-3} and 10^{-4} mol kg^{-1}.

The solution of peroxide (TBPEH or BP) and polymerizable fluorescence probe in dichloromethane was impregnated into powdered PE by stirring at room temperature for 24 hours. After removing the solvent under reduced pressure, the polymer was dried. The grafting was performed in sealed glass ampoules under argon atmosphere at 80°C for 25 hours for BP mixtrures, and 21 hours for TBPEH mixtures. After opening the ampoules, the polymer was extracted three times with ethanol to remove unreacted probe and then with diethyl ether to remove peroxide. The amount of ungrafted probe was determined by relating the absorbance of pyrene moiety in the combined ethanol extracts to a calibration curve of the respective pyrene probe in ethanol. The amount of grafted probe was determined from the difference of absorbance of charged probe and that of the ungrafted probe. The amount of grafted probe for PyMMA and PyBMA was established 7.5×10^{-4} mol kg^{-1}, for PyMMS 7×10^{-4} mol kg^{-1} and for allyl-type monomer PyMAE 6.1×10^{-4} mol kg^{-1}.

Techniques

Absorption spectra were taken on a M-40 UV-VIS (C. Zeiss, Jena, Germany). Emission spectra were recorded on a Perkin-Elmer MPF-4 spectrofluorimeter (Perkin-Elmer, Norfolk, CT) which was connected through interface and A/D converter to a microcomputer [14] for data collection, processing and plotting on an XY 4110 plotter (Laboratorní prístroje n.e., Prague, CR). Emission of solutions was measured at right angle in a 1 cm cell. The quantum yields were determined relative to anthracene in cyclohexane or methanol. Emission of polymer films was measured in front-face arrangement to the solid sample holder. The quantum yield of polymer films was determined using anthracene as standard and assuming its insensitivity to the medium. The quantum yields in solution and in film were determined according to the relation [15]:

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

where Φ^S_F is the quantum yield of standard, integrals $\int_0^\infty I_F(\nu)d\nu$ and $\int_0^\infty I_F^S(\nu)d\nu$ are the areas under curves of the probe and standard, respectively, A and A^S are absorption of the probe and standard.

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 (λ = 337 nm) and emission was selected by the use of cut-off filters. The output signal was digitized and transferred to a microcomputer [16]. Since the fluorescence lifetimes of pyrene and its derivatives are >10× 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 [17]. The standard deviation, $G^{1/2} = \Sigma((I_{exp} - I_{calc})^2/n)^{1/2}$, 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 minutes). All measurements on polymer films were done in the presence of air.

All relevant spectral data of pyrene based probes in various media are given in Tables 1 and 2.

RESULTS AND DISCUSSION

The prepared monomers according to Scheme 1 exhibit characteristic absorption spectra for pyrene (Figure 1). Substitution on the pyrene ring does not result in substantial modification of absorption bands of parent pyrene and no new bands are formed. The maxima of absorption of bands are shifted bathochromically about 10 nm as compared with pyrene (Table 1). The vibrational structure is the same in solution as well in polymer matrices. In going from polar methanol to non-polar cyclohexane, better vibrational resolution is observed as well as slight red shift (about 2 nm). No difference in position of absorption maximum is

Table 1. Absorption Characteristics of Pyrene Derivatives in Different Environments

Probe	Medium[a]	λ_{max}[b] [nm]	logε[c] [dm^3 mol^{-1} cm^{-1}]
Pyrene	Me	294, 304, 316, 332	4.77
	Cy	294, 305, 318, 334	4.53
	Chloroform	308, 321, 336	4.64
	PE	298, 308, 322, 337	4.18
	PS	301, 312, 325, 340	4.40
	PMMA	308, 321, 336	4.78
	PVC	311, 323, 339	4.51
	IPN	299, 312, 327	4.30
1-pyr-CH_2OH	Me	297, 324, 339	4.70
	Cy	299, 312, 325, 340	4.85
	Chloroform	302, 314, 328, 344	4.64
	aPP	313, 327, 342	4.33
	PE	324, 328, 345	4.02
	PS	305, 315, 331, 346	4.25
	PMMA	313, 328, 344	4.66
	PVC	303, 314, 329, 346	4.42
	IPN	329, 346	4.52
PyMMA	Me	299, 312, 325, 339	4.66
	Cy	299, 312, 325, 342	4.58
	Chloroform	303, 314, 329, 345	4.64
	aPP	303, 314, 327, 344	4.51
	PE	303, 314, 327, 344	4.44
	grafted to PE	315, 330, 346	4.45
	PS	303, 315, 332, 346	4.42
	PMMA	313, 328, 345	4.48
	PVC	303, 316, 330, 346	4.52
	IPN	315, 330, 346	4.55
	IPN (grafted PE)	315, 330, 350	4.22
PyMMS	Me	296, 312, 323, 339	4.76
	Cy	299, 313, 325, 341	4.77
	Chloroform	303, 314, 328, 344	4.67
	aPP	300, 313, 327, 342	4.43
	PE	303, 314, 328, 345	4.52
	grafted to PE	313, 328, 345	4.20
	PS	315, 330, 346	4.24
	PMMA	313, 328, 344	4.53
	PVC	314, 329, 345	4.56
	IPN	315, 330, 346	4.56
	IPN (grafted PE)	315, 330, 347	3.76
PyBMA	Me	326, 341	4.57
	Cy	315, 327, 343	4.60
	PE	329, 346	4.37
	grafted to PE	340, 354	4.13

(continued)

Table 1. Continued

Probe	Medium[a]	λ_{max}[b] [nm]	logε[c] [dm^3 mol^{-1} cm^{-1}]
	PS	317, 331, 347	4.40
	PMMA	316, 329, 346	4.47
	PVC	319, 331, 348	4.42
	IPN	330, 346	3.88
	IPN (grafted PE)	356	3.2
PyMAE	Me	326, 342	4.57
	Cy	215, 327, 343	4.59
	PE	330, 346	3.21
	Grafted to PE	360	3.66
	PS	319, 331, 347	4.38
	PMMA	316, 329, 345	4.59
	PVC	317, 331, 348	4.49
	IPN	330, 347	4.65
	IPN (grafted PE)	328, 347	—

[a] Me: methanol, Cy: cyclohexane, aPP: atactic polypropylene, PE: polyethylene, PS: polystyrene, PMMA: polymethyl methacrylate, PVC: polyvinyl chloride, IPN: interpenetrating polymer network (PE: P(S : BMA), 1 : 1(3 : 7)). Concentration = 10^{-5} mol dm^{-3} in solution, 0.002 mol kg^{-1} in polymer film, 10^{-4} mol kg^{-1} in IPN matrice, 3×10^{-4} mol kg^{-1} in IPN with grafted PE and concentration in grafted PE are about $7–6 \times 10^{-4}$ mol kg^{-1} (see experimental section).

[b] Maximum of absorption band.

[c] Molar extinction decadic coefficient of the longest wavelength absorption band.

observed for polymer matrices of different polarity. In all matrices, the vibrational structure is preserved. The poorest vibrational resolved absorption spectra are observed in PS matrix. No distinct influence of polarity of environment on absorption of pyrene-based monomers is observed. Grafting of monomers PyBMA and PyMAE on PE brings about a red shift in absorption ca 10 nm. The same shift is observed using PE, grafted with PyBMA or PyMAE monomers, for IPN preparation (Figure 2). For other monomers, (PyMMA, PyMMS) this shift is smaller. In IPN systems containing txerpolymerized monomers, the monomers exhibit the same absorption spectrum in IPN as when freely added to other polymer matrices such as PE, PS, PMMA and PVC.

Fluorescence spectra of pyrene derivatives in solution, as well as in polymer matrices at low concentration, exhibit emission in the region 370–430 nm. (Table 2). Positions of emission maximum of these derivatives as compared with pyrene are red-shifted by about 3 nm in solutions only (Figure 3). In polymer matrices, the positions of maximum are nearly the same as in unsubstituted pyrene (Figure 4). Emission spectra of all derivatives is composed of four bands. The best resolved and the most intense bands are the first and third. The fourth band in the region 410–430 nm is weak and broad. It usually appears as a shoulder to the

Table 2. Emission Characteristics of Pyrene Derivatives

Probe	Medium[a]	λ_{em}[b] [nm]	Φ_r[c]	λ_{ex}[d]	τ[e] [ns]	$G^{1/2}$[f] [%]
Pyrene	Me	374,386,395	0.85		285.5	1.66
	Cy	375,386,395	1.95		413.6	2.06
	Chloroform	376,386,396	1.08		132.6	1.10
	PE	396	2.08		269.4	2.10
	PS	376,381,386,396	0.58	338	277.1	0.74
	PMMA	375,381,386,396	1.04		241.7	3.10
	PVC	376,381,386,396	0.98		170.3	3.10
	IPN	386,396	0.12		310.8	0.97
1-pyr-CH_2OH	Me	378,388,396	0.31	342	150.9	2.20
	Cy	376,383,389,396	1.09	"	275.0	3.20
	Chloroform	379,390,398	0.99	"	101.5	1.70
	aPP	378,390, 396	0.67	"	199.5	2.80
	PE	396	2.88	"	222.9	1.80
	PS	379,390,398	0.85	"	176.4	1.90
	PMMA	377,383,388,397,415	0.45	"	148.8	3.40
	PVC	378,388,398	1.81	"	103.8	6.20
	IPN	379,389,399	0.023	347	209.6	4.18
PyMMA	Me	377,388,396	0.13	344	138.8	7.06
	Cy	377,383,390,397	0.95	"	279.2	1.83
	Chloroform	379,389,398	2.68	"	105.7	0.94
	aPP	377,389,397	0.47	"	156.5	3.89
	PE	378,397	1.054	"	229.7	0.98
	grafted to PE	382,389,399	1.85	347	16.04[g]	0.83
	PS	378,398	0.36	344	90.77	8.81
	PMMA	377,389,397,415	0.99	"	59.53	11.4
	PVC	378,398	2.45	"	64.92	8.33
	IPN	378,398	0.169	347	181.9	3.77
	IPN grafted PE	382,401	0.173	352	15.35[g]	1.07
	S–co-BMA	378,397	0.025	347	239	1.39
PyMMS	Me	377,388,397	0.64	344	222.0	1.64
	Cy	377,383,389,398	1.24	"	302.7	2.49
	Chloroform	379,391,398	2.47	"	113.0	1.89
	aPP	379,389	0.46	"	113.1	11.1
	PE	377,397	1.69	"	238.3	1.20
	grafted to PE	380,383,389,400	0.85	347	9.86[g]	0.78
	PS	379,395	0.55	344	123.0	0.90
	PMMA	377,383,389	0.54	"	39.2	14.1
	PVC	378,383,390,398	2.2	"	63.4	10.7
	IPN	378,389,398	0.2	347	180.0	3.27
	IPN grafted PE	390,398	0.156	353	11.59[g]	1.61
	S–co-BMA	378,389,398	0.23	347	221.3	2.66
PyBMA	Me	377,396	0.12	343	161.3	4.40
	Cy	378,382,388,398	0.29	343	275.4	1.08

(continued)

Table 2. Continued

Probe	Medium[a]	λ_{em}[b] [nm]	Φ_r[c]	λ_{ex}[d]	τ[e] [ns]	$G^{1/2}$[f] [%]
	PE	378,383,388,398	0.25	347	153.6	5.18
	grafted PE	385,406	0.05	355	13.32[g]	0.59
	PS	379,385,390,400,418	0.16	349	170.8	0.95
	PMMA	378,384,388,398,416	0.24	347	160.6	2.70
	PVC	379,399	0.12	348	115.8	3.60
	IPN	378,399	0.102	347	163.3	2.32
	IPN grafted PE	384,405	0.071	355	11.01[g]	0.71
PyMAE	Me	377,396	0.2	343	278.7	0.84
	Cy	378,394	0.3	343	317.2	0.92
	PE	378,383,389,398	0.71	347	159.8	7.96
	grafted PE	389,408	0.039	360	10.49[g]	1.62
	PS	378,398	0.24	349	201.8	1.03
	PMMA	378,398	0.24	347	208.0	1.91
	PVC	378,398	0.15	348	150.1	2.80
	IPN	379,399	0.16	347	210.6	2.57
	IPN grafted PE	383,401	0.098	353	8.71[g]	1.47
	S–co-BMA	379,389,399	0.11	347	197.8	5.67

[a] Symbols are explained in Table 1.
[b] Wavelength at the maximum of emission band.
[c] Relative quantum yield to anthracene.
[d] Excitation wavelength.
[e] Lifetime determined without deconvolution.
[f] Standard deviation [%].
[g] Biexponential fitting.

strongest band at 396–399 nm. In some cases, spectra are observed with well-resolved vibrational structure emission consisting of five bands (Table 2). The band in region 386–390 nm is mostly lost in polar methanol for most derivatives. By contrast, this band is strongest for PyMMS in a majority of polymer matrices.

The vibrational structure of methacrylic derivatives of pyrene is preserved in all environments and is the same as the vibrational structure of unsubstituted pyrene. The vibrational structure PyMAE and PyMMS is partially lost in non-polar cyclohexane. In non-polar polymer matrices, these derivatives exhibit well-resolved vibrational structure. The emission intensity of the bands varies for all derivatives. It also depends on the polarity of the environment in a similar way as pyrene, which is the base for the pyrene scale [4]. It is based on the ratio of the intensity of bands at 378 and 388 nm (Figure 4). This ratio is given for prepared derivatives in different polymer media in Table 3. The values for this ratio for derivatives PyMMA, PyMMS and PyMAE reflect the polarity of polymer matrices. Based on this value, we can judge the presence of the respective probe in various regions of the IPN. These data indicate that PyMMS is copolymerized with

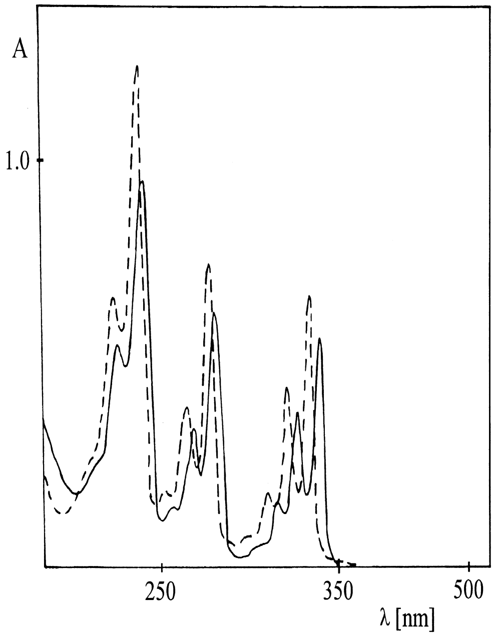


Figure 1. Absorption spectrum of (- - -)and PyMMA (——) in cyclohexane at 10^{-5} mol dm^{-3}.

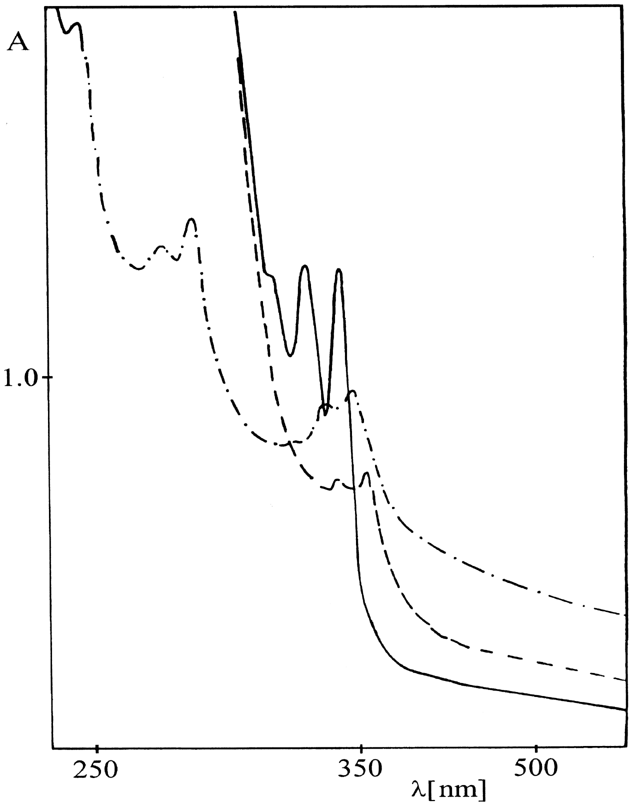


Figure 2. Absorption spectrum of PyBMA in IPN (——) at c = 10^{-4} mol kg^{-1}, thickness 2 mm, PyBMA grafted on PE, (– • – •) at c = $3\text{x}10^{-4}$ mol kg^{-1}, thickness 0.1 mm and PyBMA grafted on PE in IPN (- - -) at c = $3\text{x}10^{-4}$ mol kg^{-1}, thickness 2 mm.

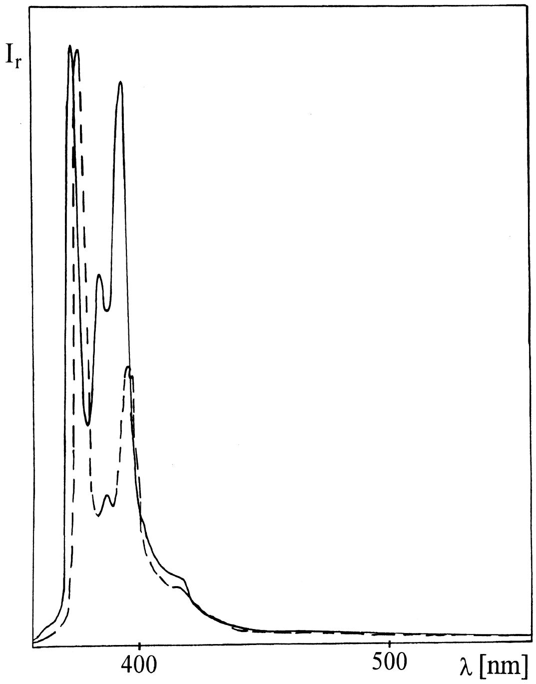


Figure 3. Emission spectrum of pyrene (——) in methanol (λ_{ex} = 338 nm) at 10^{-5} mol dm^{-3} and Py MMA (- - -) in methanol (λ_{ex} = 344 nm) at 10^{-5} mol dm^{-3}.

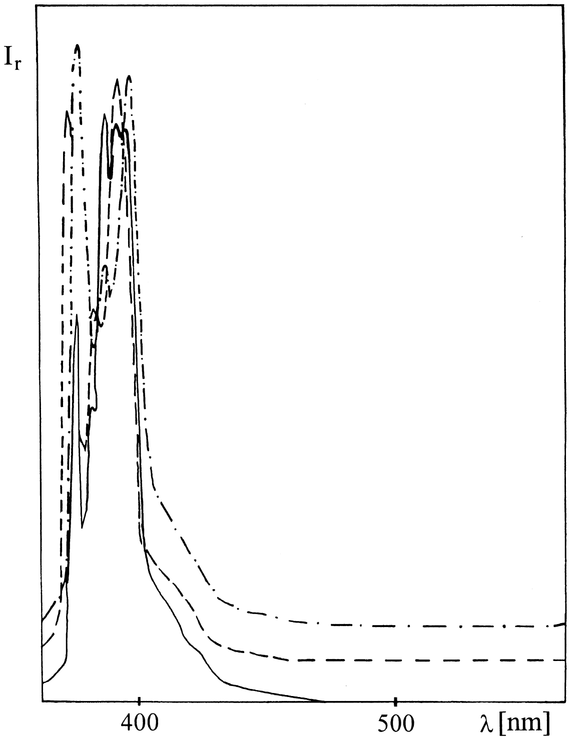


Figure 4. Emission spectrum of PyMAE (——) doped in PE at 10^{-4} mol kg^{-1}, doped in PMMA (- - -) at 2×10^{-3} mol kg^{-1} (set off) and copolymerized in IPN (– • – • –) at 10^{-4} mol kg^{-1} (set off).

Table 3. Polymer Polarity Dependence of Relative Band Intensities I_1 (378 nm)/I_3 (388 nm) in Polymer Bounded 1-Pyrenyl Compound Monomer, Fluorescence Emission, $\lambda_{ex} = 347$ nm

Probes Bounded Form	Polymer	I_1/I_3
Pyrene (doped)	IPN	1.39
PyMMA	LDPE film	1.01
	PS film	1.96
	PMMA	2.45
	PVC film	2.61
	IPN	2.30
	S : BMA (3 : 7)	2.56
PyMMS	LDPE film	0.43
	PS film	—
	PMMA film	1.17
	PVC film	1.99
	IPN	1.20
	S : BMA (3 : 7)	1.11
PyMAE	LDPE film	0.67
	PS film	0.82
	PMMA film	1.52
	PVC film	1.97
	IPN	1.46
	S : BMA (3 : 7)	0.55
PyBMA	LDPE film	6.12
	IPN	5.89

styrene and methacrylate monomers containing pyrene with butyl methacrylate. According to the value of the ratio, I_1/I_3, the monomer, PyMAE, containing the allyl group, is copolymerized mostly in the methacrylate part of the copolymer what confirm the values of the ratio, I_1/I_3, for IPN and PMMA film. The ratio, I_1/I_3, is high for PyBMA and does not change with the change of polarity in going from polar methanol to non-polar cyclohexane or from the polar methacrylate part in IPN to non-polar LDPE. Consequently, this derivative is not a suitable polarity probe (Figure 5). The same conclusion is obtained for application of 1-pyrenebutanol as polarity probe in the block copolymer styrene-2-vinylpyridine [6]. PyBMA does not reflect the polarity of the environment as does the parent alcohol. Upon grafting of monomers on PE, the shape of the emission spectra changes with respect to a non-polar environment. The most intense band in emission becomes I_3, as seen in the spectrum of PyMMS (Figure 6).

The change of the ratio S:BMA in the copolymer part of an IPN network results in change of the ratio, I_1/I_3, of bound pyrene-based fluorescence probes due to their sensitivity to change of polarity (Table 4). This means that this part of the network forms one phase and addition of styrene or butyl methacrylate influences the probe bonded in the styrene or butyl methacrylate parts of the IPN. This conclusion is in accord with observation of TEM pictures of such IPN networks

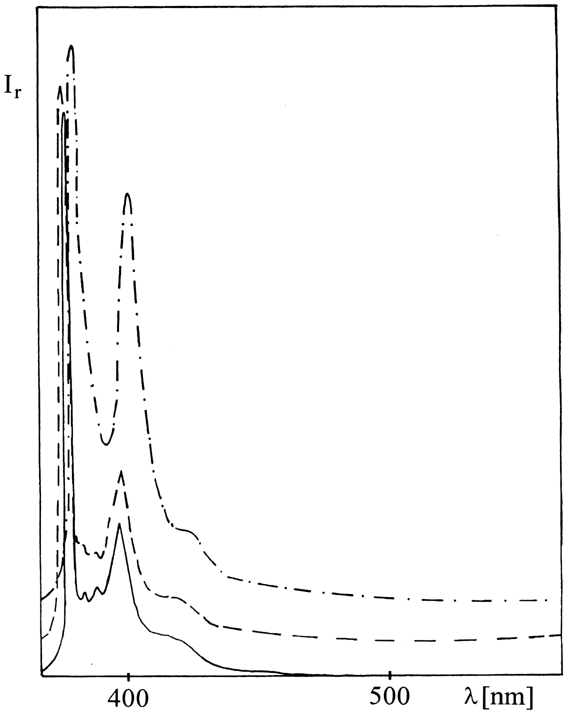


Figure 5. Emission spectrum of PyBMA (——) doped in PE at 10^{-4} mol kg^{-1}, copolymerized in IPN (- - -) at 10^{-4} mol kg^{-1} (set off) and grafted on PE in IPN (– • – • –) at $3x10^{-4}$ mol kg^{-1} (set off).

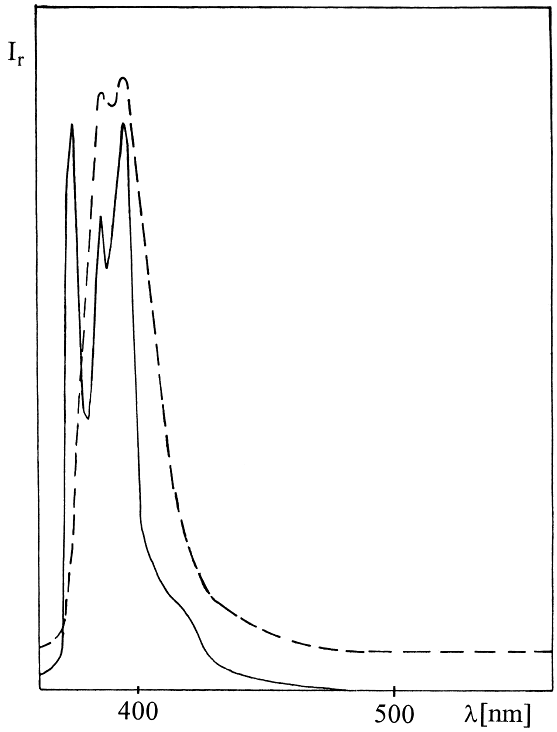


Figure 6. Emission spectrum of PyMMS (——) copolymerized in IPN at 10^{-4} mol kg^{-1} and grafted on PE in IPN (- - -) at $3x10^{-4}$ mol kg^{-1} (set off).

Table 4. Polymer Polarity Dependence of Relative Band Intensities I_1 (378 nm)/I_3 (388 nm) in Polymer Bounded 1-Pyrenyl Substitute Monomer, Emission, λ_{ex} = 347 nm

Ratio of Copolymer in IPN (S:BMA)	Pyrene Bounded Form	I_1/I_3
2 : 8	PyMMA	2.45
3 : 7		2.30
4 : 6		1.54
2 : 8	PyMMS	1.13
3 : 7		1.20
4 : 6		0.99

which show that a continuous phase is formed by PE and a dispersed phase is the copolymer BMA-co-S [18].

Upon increasing network density by the addition of the crosslinking agent BDDM to IPN, no shift, change of quantum yield or change in emission intensity of the respective bands, as well as the ratio I_1/I_3, for the PyMMA and PyMMS derivatives is observed (Table 5).

No dependence of the emission on probe concentration was observed. The emission spectra in solution were taken at a concentration of 10^{-5} mol dm^{-3}. At this concentration, no excimer emission of probes is observed. In PE films, S-co-BMA copolymer networks and IPN networks, the spectra were taken at 10^{-4} and 10^{-3} mol kg^{-1} concentration. No change in vibrational structure and position of maxima, as well as no excimer emission was observed under these conditions (Table 6).

For methacrylate monomers, namely PyMMA, PyBMA, and an allyl ether type, as PyMAE, the shape of the spectrum depends on the wavelength of excitation. This is clearly demonstrated on the spectra of these derivatives in PE, IPN and

Table 5. Emission Characteristic of Pyrene Probes in IPN with Different Network Densities, λ_{ex} = 347 nm

Probe	The Amount of Crosslinker BDDM [mol %]	$\lambda_{em}{}^{a}$ [nm]	$\Phi_r{}^{b}$	I_1/I_3
PyMMA	0.5	378, 388, 398	0.20	2.30
	1	378, 388, 398	0.17	2.30
	3	378, 388, 397	0.18	2.37
PyMMS	0.5	379, 390, 399	0.21	1.23
	1	378, 389, 398	0.20	1.20
	3	378, 389, 398	0.17	1.10

[a] Wavelength at the maximum of emission band.

[b] Relative quantum yield to anthracene.

Table 6. Dependence or Emission of Pyrene-Based Probes on Concentration of Probe in PE Films, IPN Networks and S-co-BMA Networks, λ_{ex} = 347 nm

Probe	Medium[a]	Concentration of Probe [mol kg^{-1}]	λ^{b}_{em}	Φ_r^{c}	I_1/I_3	τ^{d} [ns]
PyMMA	PE film	10^{-3}	378, 388, 397	1.10	1.21	184
		10^{-4}	378, 388, 397	2.10	1.02	184
	IPN	10^{-3}	378, 388, 398	0.22	1.73	229
		10^{-4}	378, 388, 398	0.17	2.30	247
	S-co-BMA	10^{-3}	378, 387, 397	0.16	1.87	246
		10^{-4}	378, 387, 397	0.13	2.56	239
PyMMS	PE film	10^{-3}	378, 390, 397	1.28	0.53	174
		10^{-4}	377, 387, 397	1.69	0.53	185
	IPN	10^{-3}	379, 389, 398	0.18	1.27	178
		10^{-4}	378, 383, 389, 398	0.20	1.19	180
	S-co-BMA	10^{-3}	378, 389, 398	0.18	1.13	235
		10^{-4}	378, 389, 398	0.23	1.12	221

[a] Symbols are explained in Table 1.
[b] Wavelength at the maximum of emission band.
[c] Relative quantum yield to anthracene.
[d] Lifetime determined without deconvolution.

grafted on PE. The highest intensity is observed at 353–355 nm excitation. In this case, the emission band at 389 nm is lost, and the first and third bands are 3–9 nm bathochromically shifted (Figure 5). The shape of the PyMMS emission spectrum does not depend on grafting on PE nor on the excitation wavelength (Figure 6).

The relative quantum yields of all derivatives are lower in aerated solutions than in polymer matrices. In deaerated solution they are around 0.2–1. These values of quantum yield are nearly the same as for derivatives doped in polymer films (Table 2). The highest quantum yield for all derivatives is observed in PE film in the range 1.5–2. For vinyl derivatives, a high quantum yield was observed in deaerated chloroform and PVC matrix. Grafting of monomer on PE using radical initiator, brings about a decrease of quantum yield of fluorescence, which is probably due to some chemical reaction on the pyrene ring. EPR spectroscopy indicates a low level of trapped radicals in PE matrix, and therefore, no quenching of fluorescence might be expected due to presence of free radicals. In IPN matrix, however, the relative quantum yield of chromophore bond by copolymerization and grafted on PE is nearly the same. Moreover, the relative quantum yields of bond pyrene chromophores are lower in IPN matrices as compared with polymer matrices where the chromophore is doped.

At the same time, the lifetime of the excited singlet state of grafted chromophores is substantially shorter than the lifetime of the same chromophores copolymerized or doped in polymer matrix. The lifetimes are around 10 ns and the error is large, about 15% for fitting of the decay curve to a monoexponential func-

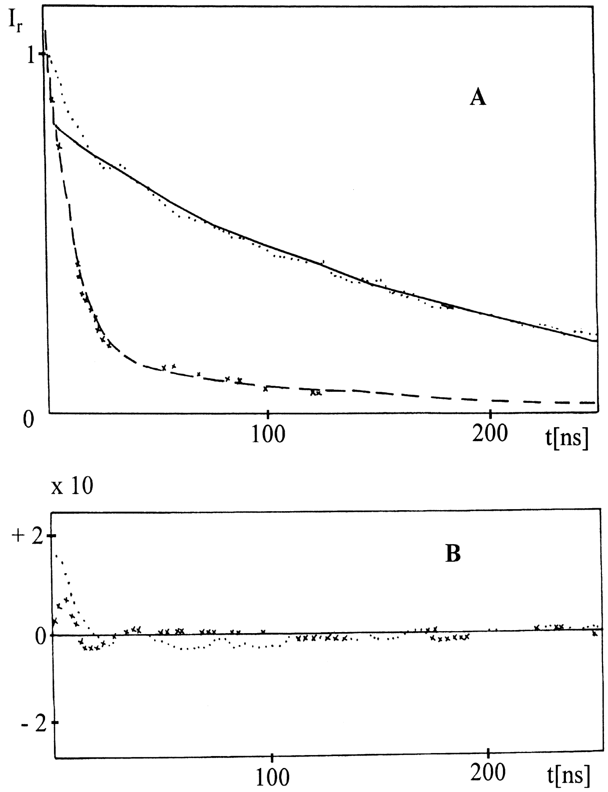


Figure 7. A: Decay curve of fluorescence of PyMMS copolymerized in IPN (——) fitted to monoexponential function and grafted on PE in IPN (- - -) fitted to biexponential function. B: Distribution of error of fitting.

tion (Figure 7). These decay curves are substantially better fitted to a biexponential function. On the other hand, the decay of fluorescence of pyrene chromophore copolymerized in IPN and doped in PE, is well-fitted to a monoexponential function. The lifetimes of the pyrene-type chromphores are shorter than for unsubstituted pyrene in the same environments. In polar matrices, the lifetimes of derivatives PyMMA and PyMMS are rather short, though at the same time, the relative quantum yields are high.

CONCLUSION

Fluorescence probes having a pyrene-type chromophore in the form of methacrylate or styrene polymerizable moiety exhibit absorption and emission spectra typical for pyrene chromophore in solution and polymer matrices. In a complex polymer system such as in IPN composed of PE and crosslinked S-co-BMA, quantum yield of fluorescence of linked probes is lower than for physically-doped probes in other solid polymer matrices. For probes PyMMA, PyMMS and PyMAE, the ratio, I_1/I_3, depends on the polarity of environment and can be exploited for characterization of the IPN. Polyethylene forms a continuous phase and fluorescence of terpolymerized probes in the S-co-BMA domain, seems not to be influenced by it. Grafting of probes on PE quantum yield of emission decreases and lifetime of fluorescence substantially shortens. This is probably due to a reaction of initiating or growing radicals with pyrene during grafting, which is a subject of further investigation.

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