Quenching of pyrene fluorescence as a technique for characterisation of swelling of interpenetrating polymer network: polyethylene/poly(styrene-co-butylmethacrylate)

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Abstract

A real-time monitoring of oxygen quenching of monomer fluorescence of bound probes: 1-pyrenemethyl methacrylate (PyMMA) and 1-pyrenemethyl(4-vinylbenzyl)ether (4-(1-pyrenyl)methoxymethylstyrene, PyMMS) was used for study of swelling of interpenetrating polymer network (IPN) consisting of polyethylene/poly(styrene-co-butylmethacrylate) (PE/P(S-co-BMA)) with different network density. The curves of oxygen quenching of pyrene chromophore were fitted to the monoexponential form of second Fick Law. The estimated diffusion coefficient of oxygen was in the range of $1–10 \times 10^{-6}$ cm^2 s^{-1} depending on the solvent and phase of IPN system. There is no dependence of fluorescence quenching by oxygen on cross-link density in this IPN systems.
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Keywords: Fluorescence; Pyrene; Quenching; Swelling; Interpenetrating network

1. Introduction

Almost all fluorophores are quenched by molecular oxygen and hence for precise measurement of quantum yields and lifetimes it is necessary to remove oxygen [1]. The most likely mechanism by which oxygen quenches molecular fluorescence is that the paramagnetic oxygen causes the fluorophore to undergo intersystem crossing to the triplet state, which is then quenched by other processes [2]. Fluorophores with lifetime under 5 ns are typically not quenched by dissolved oxygen in solution although some authors reported negligible effect of oxygen on probes with lifetime 20 ns. These values are just approximate and can be explained by diffusion. The root-mean-square distance over which a quencher can diffuse during unquenched excited state of a fluorophore is given as $(2D\tau_0)^{1/2}$ where D is diffusion coefficient and τ_0 is lifetime. Given that an oxygen molecule at 25 °C has diffusion coefficient 2.5×10^{-5} cm^2 s^{-1}, then during a typical lifetime of 5 ns the oxygen molecule can diffuse 5 nm. If the lifetime is longer, diffusion over longer distances is observed and hence there is a greater chance of quenching of the excited state of fluorophore. The rate constant of this process (k_q) is equal or near to rate constant controlled by diffusion [1]. The rate constant of quenching of S$_1$ of pyrene is 3×10^{10} M^{-1} s^{-1} and for triplet state T$_1$ is lower 2×10^9 M^{-1} s^{-1}. The mechanism of this process occurs through biradicals [1,2]:

$$M^* + O^{\cdot}\!-\!O^{\cdot} \rightarrow M^+ + O_2^{\cdot -} \rightarrow M + {}^1O_2 \rightarrow M + {}^3O_2$$
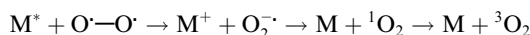
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$$M^* + O^{\cdot}\!-\!O^{\cdot} \rightarrow M^{\cdot}\!-\!O\!-\!O^{\cdot} \rightarrow M + {}^1O_2 \rightarrow M + O_2$$
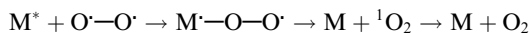
The values of k_q depend on electron donor properties of the molecule to be quenched that is they are determined by ionization potential.

Pyrene and its derivatives are widely used for monitoring of different processes in nano-size range materials as oligomers, polymers or its aggregates and micelles [3,4]. The pyrene derivatives are especially suitable for this purpose because several its spectral parameters are strongly medium dependent. Noteworthy are the vibrational structure of fluorescence [4], the ability to form homo- or hetero-dimers in excited state (excimers, exciplexes) and long lifetime of the singlet state, which are the parameters strongly dependent on macro- or micropolarity of the environment. Therefore, pyrene or its derivatives might be used as probes to be quenched by oxygen [3,4].

The synthesis, thermal and optical properties, and dynamic-mechanical behaviour of interpenetrating polymer network (IPN) composed of PE/P(S-co-BMA) have been previously reported [5,6]. The IPN system described here has been prepared with the (molar) composition of low density polyethylene (PE) and poly(butyl methacrylate-co-styrene) of 1:1, (molar ratio of BMA to S was 7:3). It is optically transparent at room temperature, although the system is heterogeneous. Recently, we have employed linked fluorescent probes based on pyrene [7] for spectral characterisation of this type of IPN.

In this paper we report the novel approach in monitoring of swelling of this IPN using steady-state fluorescence technique. Real-time fluorescence quenching was employed for monitoring swelling of IPN by aerated solvents as toluene or cyclohexane. In this way we have tried to characterise IPN blocks of different cross-link density. A range of cross-link densities was achieved by utilising various 1,4-butanediol dimethacrylate concentrations in the original IPN preparations.

2. Experimental part

2.1. Materials

The structures of the fluorescent probes used in this paper are shown in Scheme 1. The synthesis of the derivative 1-pyrenemethyl methacrylate (PyMMA) (yellow crystals with m.p. 99.5–101.5 °C) was performed by re-esterification reaction of methyl methacrylate with the 1-pyrenemethanol using tetrabutylorthotitanate (TBOT) as re-esterification catalyst as we described earlier [7]. The derivative 4-(1-pyrenyl)methoxymethylstyrene (PyMMS) (white crystals with m.p. 74–75 °C) was prepared from 1-pyrenemethanol and 1-(chloromethyl)-4-vinylbenzene under conditions for phase-transfer reaction [7,8].

The monomers used for IPN and poly(methyl methacrylate) (PMMA) sheets preparation were purified before use. The inhibitor of polymerisation was removed from butyl methacrylate (Merck, Schuchardt, Germany, 99%), styrene (Chemapol, Prague, CR) and methyl methacrylate (Chemapol, CR) monomers by washing with aqueous sodium hydroxide (5 wt.%) and water. After drying with Na_2SO_4, the monomers were distilled under reduced pressure. Low density polyethylene (Bralen 2-19, MFI 1.7–2.3 g/10 min, Slovnaft, Bratislava, SR) was the one of the component in the IPN. The cross-linker, 1,4-butanediol dimethacrylate (BDDM) (Aldrich, Steinheim, Germany, 95%) was used for cross-linking in IPN preparation as received. As initiator for IPN formation, 2,5-dimethyl-2,5-di-(*tert*-butylperoxy)hexane (Luperox 101) (Luperox GmbH, Germany) and for grafting dibenzoylperoxide (BP) (Merck, Schuchardt, Germany, 75%) were used as received.

Anthracene (Lachema, Brno, CR), used as fluorescence standard, was zonally refined. Analytical grade toluene (Lachema, Brno, CR) was distilled and dried over molecular sieve before using. Cyclohexane (Merck, Darmstadt, Germany), UV spectroscopy grade solvent, was used as received.

1-pyrenemethyl methacrylate
PyMMA

4-(1-pyrenyl)methoxymethyl styrene
PyMMS
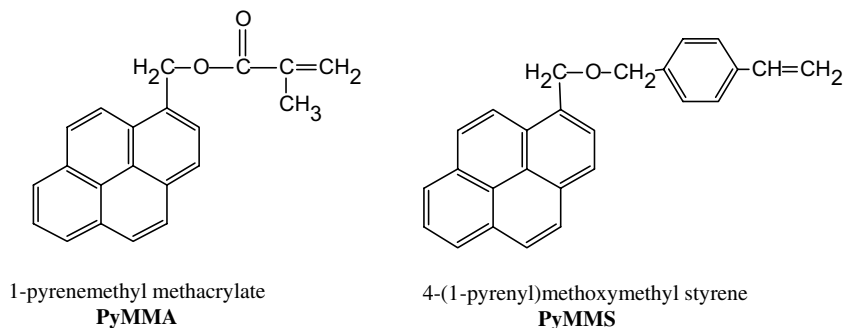
Scheme 1. Structure of fluorescence probes.

2.2. Preparation of samples

IPN samples were prepared by the same way as we described earlier [6,7]. Polymerisable probes PyMMA and PyMMS were dissolved together with LDPE in the mixture of liquid BMA, S, cross-linker and initiator. Concentration of probes was either 10^{-4} or 10^{-3} mol kg^{-1} calculated on mass of IPN. The molar ratio PE to monomer was kept equal to 1:1 and monomer ratio BMA:S was 7:3. A small amount of inhibitor of polymerisation (benzoquinone, 0.15 ml of solution 1.9×10^{-2} mol dm^{-3} of benzoquinone in styrene) was also added to prevent thermal polymerisation while dissolving PE in monomers at 110 °C. For all samples, 2 wt.% Luperox 101 as initiator of polymerisation and either 0.5, 1 and 3 mol% BDDM as cross-linking agent, were added. The resulting solution was poured between two glass plates, sealed on three sides by the silicon rubber tubing, from top covered by paper tape to prevent evaporation of monomers and put in the oven. The reaction was carried out at 110 °C for 5 h, followed by 1 h at 160 °C. The samples with grafted probes to PE before were prepared by the same way. The samples of PMMA cross-linked blocks with linked or doped fluorescence probes were prepared by a similar block polymerisation of solution of probes, initiator and cross-linker in monomer. The thickness of the IPN and PMMA blocks was ≈2 mm.

For grafting of fluorescence probes to LDPE as one phase of IPN, we used peroxide initiated grafting method in solid phase [9]. The solution 1×10^{-2} mol kg^{-1} of BP and fluorescence probe (10^{-3} mol kg^{-1}) in dichloromethane were impregnated into powdered PE during stirring at room temperature for 24 h. After removing the solvent under reduced pressure, the polymer was dried. Grafting was performed in the sealed glass ampoules under argon atmosphere at 80 °C for 25 h (7 half-times of decomposition of BP). After opening the ampoules, the polymer was extracted three times with ethanol to remove non-reacted probe and then with diethyl ether to remove peroxide and its decomposition products. The amount of gel of PE, formed at grafting reaction using 1×10^{-2} mol kg^{-1} of BP, has been fixed on 1.5% (toluene extraction in Soxhlet apparatus). The amount of non-grafted 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 grafted probe and that of the non-grafted probe. The amount of grafted probe for PyMMA was found to be 7.5×10^{-4} mol kg^{-1}, and for PyMMS 7×10^{-4} mol kg^{-1}.

2.3. Techniques

Absorption spectra were taken on a M-40 UV–VIS (C. Zeiss, Jena, Germany). Steady-state emission spectra were recorded on a Perkin–Elmer MPF-4 spectrofluorimeter (Perkin–Elmer, Norfolk, CT, USA), which was connected through interface A/D converter to a microcomputer [10] for data collection, processing and plotting on an XY 4110 plotter (Laboratorní přístroje, Prague, CR) or to PC computer for time dependent measurements. Emission of dry IPN samples was measured in front-face arrangement in the solid sample holder. Real-time monitoring of emission of swelled IPN blocks with linked fluorescence probes were measured using a front-face arrangement in crossed position in a 1×1 cm cuvette at 40 °C according to Scheme 2.

The quantum yield of polymer films was determined using anthracene as standard and assuming its low sensitivity to the medium [11]. Anthracene was used as standard because it was soluble and compatible with the different matrices used. For our purpose this kind of comparison was sufficient. Fluorescence lifetime measurements were performed on a LIF 200 (Lasertechnik Ltd., Berlin, Germany) which operates as a stroboscope. The excitation source was a pulsed nitrogen laser (100 kW ≈20 Hz, $\lambda = 337$ nm) and emission was selected by the use of 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× 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, $G^{1/2} = \sum((I_{exp} - I_{calc})^2/n)^{1/2}$, 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 10 min). However, all measurements on polymer films and real-time measurements of quenching of swelled IPN were done in the presence of air. All relevant spectral data of pyrene based probes in various media are given in Table 1.
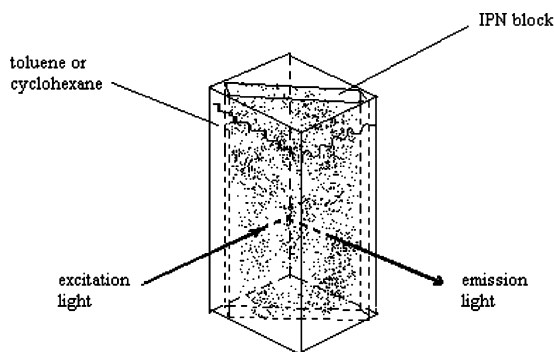
Scheme 2. Arrangement of the sample in the cuvette.

Table 1
Complex spectral characteristics of pyrene probes in different media

Probe	Medium[a]	λ_{abs}[b]	λ_{em}[c] [nm]	Φ_r[d]	λ_{ex}[e]	τ[f] [ns]	$G^{1/2}$[g] [%]
PyMMA	Me	339	377,388,396	0.13	344	138.8	7.06
	Cy	342	377,383,390,397	0.95	”	279.2	1.83
	Chloroform	345	379,389,398	2.68	”	105.7	0.94
	aPP	344	377,389,397	0.47	”	156.5	3.89
	PE	344	378,397	1.054	”	229.7	0.98
	grafted to PE	346	382,389,399	1.85	347	16.04[h]	0.83
	PS	346	378,398	0.36	344	90.77	8.81
	PMMA	345	377,389,397,415	0.99	”	59.53	11.4
	PVC	346	378,398	2.45	”	64.92	8.33
	IPN	346	378,398	0.169	347	181.9	3.77
	IPN (g-PE)	350	382,401	0.173	353	15.35[h]	1.07
	S-co-BMA	–	378,397	0.025	347	239.5	1.39
PyMMS	Me	339	377,388,397	0.64	344	222.0	1.64
	Cy	341	377,383,389,398	1.24	”	302.7	2.49
	Chloroform	344	379,391,398	2.47	”	113.0	1.89
	aPP	342	379,389	0.46	”	113.1	11.1
	PE	345	377,397	1.69	”	238.3	1.20
	grafted to PE	345	380,383,389,400	0.85	347	9.86[h]	0.78
	PS	346	379,395	0.55	344	123.0	9.90
	PMMA	344	377,383,389	0.54	”	39.2	14.1
	PVC	345	378,383,390,398	2.2	”	63.4	10.7
	IPN	346	378,389,398	0.2	347	180.0	3.27
	IPN (g-PE)	347	390,398	0.156	353	11.59[h]	1.61
	S-co-BMA	–	378,389,398	0.23	347	221.3	2.66

[a] Me: methanol, Cy: cyclohexane, aPP: atactic polypropylene, PE: polyethylene, PS: polystyrene, PMMA: poly(methylmethacry-late), PVC: poly(vinylchloride), 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 matrices, 3×10^{-4} mol kg^{-1} in IPN with grafted PE and concentration in grafted PE are about 7.5 and 7×10^{-4} mol kg^{-1} (see experimental section).

[b] Longest-wavelength absorption band.

[c] Wavelength at the maximum of emission bands.

[d] Relative quantum yield to anthracene. The estimated error is ±20%.

[e] Excitation wavelength.

[f] Fluorescence lifetime evaluated as monoexponentials without deconvolution.

[g] Standard deviation [%].

[h] Biexponential fitting.

3. Results and discussion

Spectral characterisation of pyrene fluorescence probes PyMMA and PyMMS in liquid and solid media has been performed previously in some details [7]. These probes in solvents and solid polymer matrices as well as attached to copolymer part (BMA-co-S) or to PE part of IPN matrix exhibit monomer fluorescence emission typical for pyrene moiety with maxima in region 378–401 nm (Figs. 1 and 2 and Table 1). Intensity of fluorescence, expressed as quantum yield of fluorescence, were lower in IPN as compared with other polymer matrices as polystyrene or poly(methyl methacrylate). An influence of cross-links density of dry network on the intensity of emission of the probes has not been observed (Table 2). The same data have been observed for more densely cross-linked poly(methyl methacrylate)

solid matrix. This confirms, that IPN block is a typical solid polymer matrix in glassy state.

Both probes (PyMMA and PyPMMS) exhibit broad range of lifetimes in different media (Table 1), the longest lifetime being in non-polar cyclohexane as solvent (around 300 ns) and polyethylene solid matrix (around 250 ns). In IPN, prepared by standard procedure, the lifetime is around 200 ns. During swelling the lifetime is shortened below 20 ns but measuring the lifetime is not feasible technique to monitor swelling. The probes grafted on PE exhibit rather short lifetime in PE film as well as in IPN (around 20 ns). In spite of this the fluorescence of IPN with grafted probes is quenched by aerated solvent.

Different behaviour results in the case when the matrix containing bound probe is swollen in the solvent. The intensity of emission is quenched by penetrating
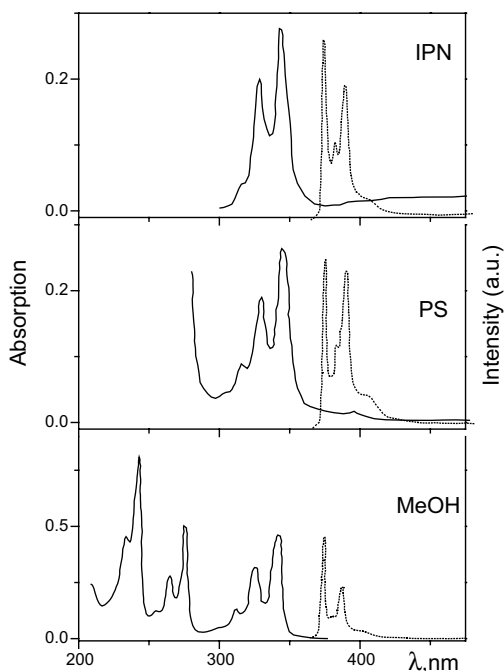
Fig. 1. Absorption and emission spectra of PyMMA in MeOH (10^{-5} mol dm^{-3}), in PS (0.002 mol kg^{-1}) and IPN (10^{-4} mol kg^{-1}).
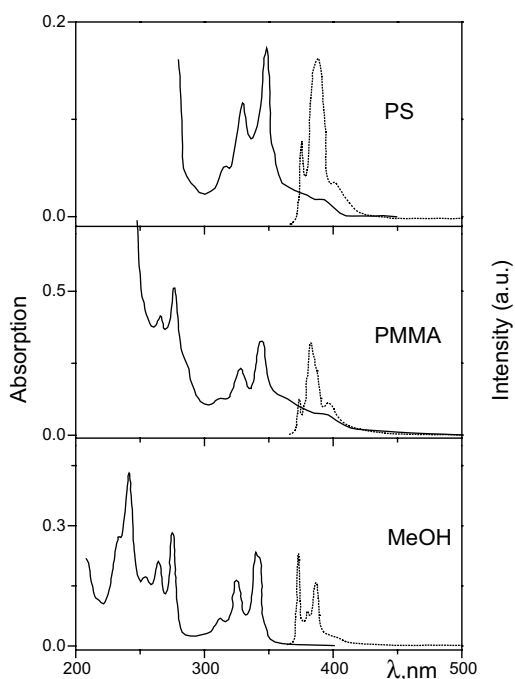

Fig. 2. Absorption and emission spectra of PyMMS in MeOH (10^{-5} mol dm^{-3}), in PMMA (0.002 mol kg^{-1}) and in PS (0.002 mol kg^{-1}).

Table 2
Influence of network density on quantum yield of fluorescence of unsubstituted pyrene and PyMMA

Probe	Medium[a]	Mol% BDDM	λ_{em}[b]	Φ_r[c]
Pyrene	PMMA network	0.5		0.27
		1	375 385 395	0.20
		3		0.23
		5		0.27
PyMMA	Cyclohexane	–	377 383 390 397	0.95
	IPN	0.5		0.15
		1	378 398	0.17
		3		0.12
	PMMA film	–	377 389 397 415	0.99
	PMMA network	0.5		0.25
		1	377 387 397	0.30
		3		0.25
		5		0.24

[a] The symbols are: PMMA—poly(methylmethacrylate), IPN—interpenetrating polymer network (PE/P(S-co-BMA), 1/1 molar ratio).

[b] Fluorescence emission maxima.

[c] Relative quantum yield to anthracene. The estimated error ±20%.

solvent which influences the excited state of fluorophore, and also by the penetrating oxygen which quenches the long lived excited state of pyrene chromophore. The rate of penetrating solvent is influenced by the cross-links density of the matrix.

Oxygen is present in all aerated organic solvents. Its ability to quench the fluorescence of pyrene derivatives is employed to differentiate various phases in IPN matrices. The solubility of oxygen in common organic solvents at laboratory temperature is around 10^{-3} mol dm^{-3} (cyclohexane 2.3×10^{-3} mol dm^{-3} and toluene 1.91×10^{-3} mol dm^{-3}) [14]. Swelling of IPN matrix by aerated toluene or cyclohexane allows the oxygen to be transported in the neighbourhood of pyrene and to quench its fluorescence. The variation in rate of penetration in polymer networks depends on network cross-links density as well as the affinity of the solvent for the various polymer matrices. Solvents probably do not swell all phases of IPN uniformly. Cyclohexane swells mainly PE phase (permeation in LDPE at 54 °C is 1470 g mm/(m^2 24 h)), but in some extent the copolymer as well. Toluene swells mainly copolymer phase but at the same time its penetration into PE phase is higher than cyclohexane (permeation in LDPE at 54 °C is 2270 g mm/(m^2 24 h)) [15].

IPN network containing bound PyMMA probe and swollen by cyclohexane at 40 °C shows no difference in rate of quenching between IPN with lower cross-links density (0.5 mol% BDDM) and higher cross-links
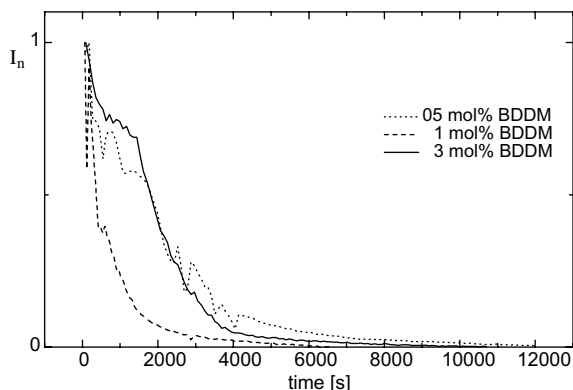
Fig. 3. Quenching of fluorescence intensity of PyMMA ter-polymerised in IPN (PE:P(S:BMA), 1:1(3:7)) with different network density and swelled in cyclohexane at 40 °C. $\lambda_{ex} = 347$ nm, emission wavelength 377 nm.

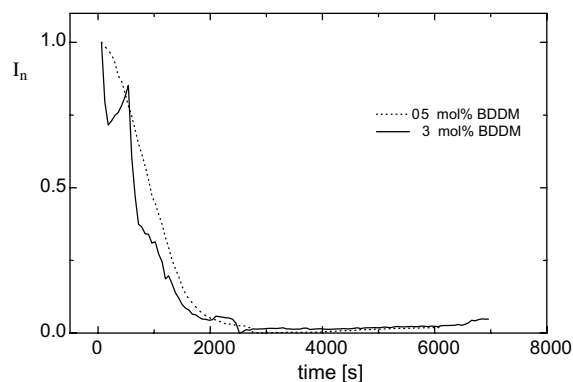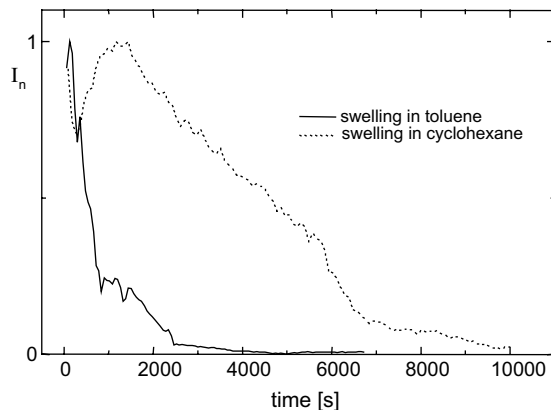Fig. 5. Influence of quality of solvent on quenching of fluorescence PyMMS terpolymerised in IPN (PE:P(S:BMA), 1:1(3:7)) (3 mol% BDDM) at swelling of IPN network, $\lambda_{ex} = 347$ nm, emission wavelength 388 nm.

Fig. 4. Quenching of fluorescence intensity of PyMMS grafted to PE phase of IPN (PE:P(S:BMA), 1:1(3:7)) with different network density and swelled in toluene at 40 °C. $\lambda_{ex} = 353$ nm, emission wavelength 398 nm.

density (3 mol% BDDM) (Fig. 3). Similar results were obtained for cyclohexane swelling of IPN containing the second type of probe, PyMMS. Although toluene is more effective swelling agent, no difference is observed based on quenching fluorescence data in swelling rate of IPN matrices with different cross-links density (Fig. 4). This result points out that BDDM cross-links preferentially the BMA-co-S phase without probe.

The decrease of monomer fluorescence intensity of bound pyrene probe at swelling of IPN should be more rapid with toluene as solvent at 40 °C. In fact gravimetric method indicates that toluene swells IPN more than cyclohexane and therefore it should better facilitate oxygen diffusion. In this way more oxygen is transported to the neighbourhood of pyrene resulting in a larger extent of quenching. The dependence of fluorescence intensity on time (Fig. 5) indicates that this process de-

pends on quality of the solvent and does not depend solely on the rate of oxygen penetration.

This dependence of fluorescence intensity on time was not well reproducible in all cases. The calculated diffusion coefficient of oxygen by integral form of second Fick Law according to Eqs. (1) and (2) [16] is probably strongly influenced by solvent. In equations was the ratio C_t/C_0 substituted by $(I_t - I_\infty)/(I_0 - I_\infty)$, where I_0, I_t and I_∞ fluorescence intensity at time 0, t and ∞, l is the thickness of the sample and D is diffusion coefficient of oxygen in the given medium. The experimental setup did not allow us to determine the influence of solvent alone without oxygen on fluorescence intensity at swelling. In all experiments the system was not stable at the beginning (Figs. 3–5) and therefore the value of I_0 was not determined from the plot. Instead it was determined by extrapolation from linear dependence of fluorescence intensity on square root of time.

$$\frac{I_t - I_\infty}{I_0 - I_\infty} = \frac{8}{\pi^2} \sum_{n=0}^{15} \frac{1}{(2n+1)^2} e^{-D(2n+1)^2 \pi^2 t/l^2} \tag{1}$$

$$\frac{I_t - I_\infty}{I_0 - I_\infty} = \frac{8}{\pi^2} \left\{ f_{D_1} \sum_{n=0}^{15} \frac{1}{(2n+1)^2} e^{-D_1(2n+1)^2 \pi^2 t/l^2} \right.$$
$$\left. + (1 - f_{D_1}) \sum_{n=0}^{15} \frac{1}{(2n+1)^2} e^{-D_2(2n+1)^2 \pi^2 t/l^2} \right\} \tag{2}$$

Eq. (2) is modified form of Eq. (1), which defines two diffusion coefficients at two different sites. The fraction of the sites is f_{D_1} and $1 - f_{D_1}$. Consequently, two processes occur indicating some degree of inhomogeneity.

Curves of quenching of fluorescence of bound probes with oxygen at swelling of IPN network at 40 °C were fitted to Eq. (1) (Fig. 6). Thus diffusion coefficient of
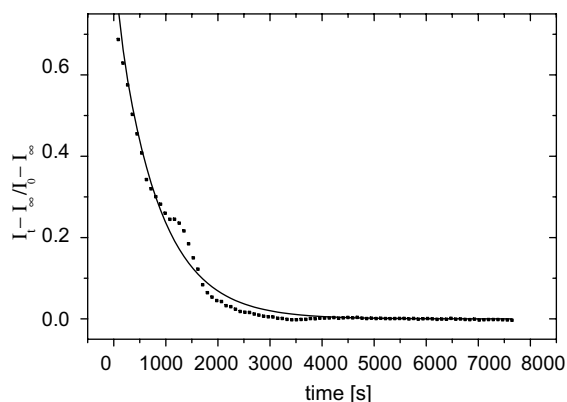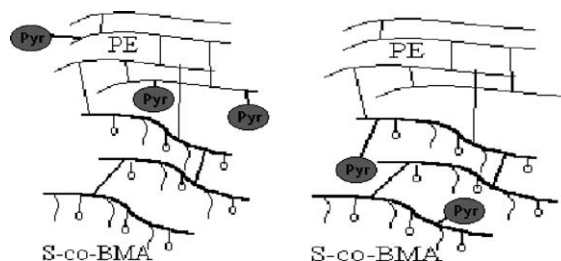
Fig. 6. Dependence of $I_t - I_\infty / I_0 - I_\infty$ on time for PyMMS terpolymerised in S-co-BMA phase of IPN (0.5 mol% BDDM) swelled in aerated cyclohexane at 40 °C (dotted line) and fitting according to Eq. (1) (full line), $\lambda_{ex} = 347$ nm, $\lambda_{em} = 388$ nm.

Scheme 3. The structure of IPN with different way of binding the probes.

oxygen was determined for different phases of the IPN system (Table 3).

Higher values of diffusion coefficients of oxygen were obtained when toluene was used as swelling solvent. This indicates that toluene penetrates more rapidly into IPN. Some differences were observed in diffusion coefficient for IPN's labelled with the same probe and in the same solvent but at different cross-link density (Scheme 3 and Table 3). These differences do not correspond the expectation a smaller D for O_2 in more dense network. This suggests that this is not an important factor in respect to the complexity of the system or higher concentration of cross-linking agent in IPN results in some structural changes. Furthermore, a higher concentration of cross-linking agent in IPN may result in some structural changes. Quenching of PyMMS linked to PE shows a small difference in diffusion of oxygen in all solvents, although the permeation of toluene is more efficient than cyclohexane. Calculated diffusion coefficients of oxygen in PE phase of IPN have higher values as we expected (D for standard LDPE at 25 °C is

4.6×10^{-7} cm^2 s^{-1}) [15]. This indicates, that cross-linking of this phase of IPN has smaller effect at higher temperature of diffusion and smaller crystallinity of PE in our IPN. All diffusion coefficients were calculated by fitting to monoexponential form of second Fick's Law (Eq. (1)). Fitting to biexponential form was not possible in the case of quenching of fluorescence of probes linked to copolymer part. This means that diffusion of oxygen to copolymer BMA-co-S is more or less equal even if S and BMA blocks are present in this statistical copolymer (permeation of O_2 into PS at 25 °C is 1.9×10^{-13} cm^3 cm/ (cm^2 s Pa)). (This value can be easily converted to 166.3 cm^3 mm/(m^2 24 h atm), standard temperature (273.15 K) and pressure (1.015×10^{-5} Pa) [17].)

The intensity ratio, $I_0 - I_\infty / I_0$, in Table 3 shows the extent of chromophores quenched by oxygen. The values near 1 indicate that all molecules of pyrene are quenched.

In a similar study [18] of quenching of fluorescence of linked pyrene in the same IPN network by penetration of the quencher diethyl oxalate (DEO) at 50 °C, the diffusion coefficient of this solvent into IPN marked by PyMMA was determined $(3.58 \pm 0.39) \times 10^{-7}$ cm^2 s^{-1} and in IPN marked by PyMMS was 4.42×10^{-7} cm^2 s^{-1}. DEO penetrates into copolymer phase of IPN. Its permeation in PE at 21.1 °C is low (0.28 g mm/(m^2 24 h)) [15]. In spite of low penetration of DEO in PE, quenching of fluorescence of pyrene linked on PE was

Table 3
Diffusion coefficients of oxygen to IPN during swelling of IPN at 40 °C and ratio of fluorescence intensities ($I_0 - I_\infty / I_0$)

Probe and place of linking in IPN	Mol% BDDM	Solvent	D (cm^2 s^{-1})	χ^2	$I_0 - I_\infty / I_0$
PyMMA copolymerised	1	Cyclohexane	$2.68 \pm 0.05 \times 10^{-6}$	7.4×10^{-4}	0.998
PyMMA copolymerised	1	Toluene	$1.49 \pm 0.02 \times 10^{-6}$	9.9×10^{-4}	0.952
PyMMA copolymerised	3	Cyclohexane	$6.03 \pm 0.07 \times 10^{-6}$	1.7×10^{-4}	0.994
PyMMA grafted on PE	3	Toluene	$9.75 \pm 0.15 \times 10^{-6}$	3.7×10^{-4}	0.995
PyMMS copolymerised	0.5	Cyclohexane	$8.78 \pm 0.14 \times 10^{-6}$	3.8×10^{-4}	0.996
PyMMS copolymerised	3	Cyclohexane	$2.05 \pm 0.04 \times 10^{-6}$	2.9×10^{-3}	0.991
PyMMS copolymerised	3	Toluene	$1.00 \pm 0.03 \times 10^{-5}$	5.5×10^{-4}	0.996
PyMMS grafted on PE	0.5	Cyclohexane	$5.61 \pm 0.16 \times 10^{-6}$	1.2×10^{-3}	0.997
PyMMS grafted on PE	0.5	Toluene	$6.57 \pm 0.13 \times 10^{-6}$	6.7×10^{-4}	0.995

observed. This might be caused by swelling with DEO of PE phase of IPN at the higher temperature. An alternative explanation takes into account fact that DEO swells interpenetrating phase where PE chains with linked pyrene are located and consequently quenching occurs. In this study [18] the curves of fluorescence quenching of pyrene linked to PE were fitted to monoexponential (Eq. (1)) because swelling process occurs in one phase of IPN. Fitting of data based on fluorescence quenching of pyrene linked to copolymer was better to biexponential (Eq. (2)). In this case the calculated diffusion coefficients describe swelling of interpenetrated BMA-co-S component of IPN.

In conclusion, these data indicates that fluorescence quenching is possible at least to estimate the diffusion coefficient of oxygen in swollen polymer. These data, however, are influenced to high degree by considerable dependence on type of solvent and swelling does not occur homogeneously. The quality of solvent is not decisive for oxygen diffusion. Solvent, which transports oxygen, supports at the same time its diffusion. The fluorescence quenching by oxygen of the linked probes does not depend on cross-links density of this type of IPN systems.

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