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# Monitoring of swelling of interpenetrating polymer network of polyethylene/poly(styrene-*co*-butylmethacrylate) (PE/P(S-*co*-BMA)) in toluene and cyclohexane using fluorescence spectroscopy

Martin Danko*, Pavol Hrdlovič, Eberhard Borsig

*Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 36 Bratislava, Slovak Republic*

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**Abstract**

A real-time monitoring of excimer emission fluorescence probe di(1-pyrenemethyl)ether (DiPyM) was used for study swelling interpenetrating polymer network (IPN) consisting of polyethylene/poly(styrene-*co*-butylmethacrylate) (PE/P(S-*co*-BMA)) and containing different network density. DiPyM was introduced into IPN during polymerisation or was penetrated into blocks from toluene solution. The effect of solvent quality for swelling of IPN and density of IPN network was also studied. From steady-state measurements of monomer and excimer emission ratio ($I_e/I_m$), no difference was found between rate of swelling IPN with 0.5, 1 and 3 mol% of cross-linker. The rate of IPN swelling seems to be rather high. Some differences was found at real-time monitoring of excimer emission ($\lambda_{em} = 495$ nm) of DiPyM measured during desorption of DiPyM from swelled IPN blocks. At higher content of cross-linker, a slower rate of DiPyM desorption from IPN matrix was observed.


*Keywords:* Fluorescence; Swelling; Interpenetrating network

## 1. Introduction

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 [1,2]. The pyrene derivatives are especially suitable for this purpose because several its spectral parameters are strongly medium dependent. Most noteworthy of these parameters are the dependence of vibrational structure of fluorescence on micropolarity of the environment [2], the ability to form homo- or hetero-dimers in excited state (excimers, exciplexes) and long lifetime of the singlet state in non-polar media (ca. 400 ns).

Formation of homo- (excimers) and heterodimers (exciplexes) of chromophores like pyrene in excited state is a well-known process and it is exploited for characterisation of microenvironment and structures of different systems (membranes, liquid crystalline and semicrystalline polymers, etc.) [1,2]. Formation of dimers can occur as inter- or intramolecular process by approaching of two species, one in excited state, dynamically or statically from preformed (chemically attached) pairs.

Bichromophoric pyrene probes, where chromophore are linked by short chain, show dynamic excimer emission even at high dilution in low viscosity isotropic solution. In high viscosity solutions or in the solid phase, this emission is completely suppressed when this process depends on some movement, e.g. rotation. On the other hand, the excimer formation for such probes can occur on preformed sites in polymer matrices, as is the case of bichromophoric probe α,ω-di(1-pyrene)alkanes in high density polyethylene [3]. Another bichromophoric probe, di(1-pyrenylmethyl) ether (DiPyM) exhibits similar spectral behaviour as di(1-pyrenyl)alkanes. Its spectral characteristics in liquid and polymeric media have been described recently [4]. This study shows that polarity and stiffness of medium do not influence the intensity of the monomer fluorescence of the probe, which is exclusively observed in polymeric media. The lifetime of monomer fluorescence in all media lies in the interval 120–200 ns. Excimer fluorescence of this probe is exclusively observed in low viscosity solvents and its

* Corresponding author. Tel.: +421-2-5477-3448; fax: +421-2-5477-5923.

*E-mail address:* upoldan@savba.sk (M. Danko).

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lifetime is in polar or non-polar solvents is in the range 40–60 ns.

Swelling and dissolution of glassy polymers can be divided into three steps [5,6]. In the first step, diffusion of the solvent occurs into polymer matrix. In the second step, relaxation of polymer chains and gel formation occurs. The relaxation of the chains is the rate limiting process. The third step is releasing of polymer chains and additive from gel into liquid phase of the solvent. Enscore et al. [5,7] proposed a model for swelling and dissolving, which does not fit Fick's law (case I) but it is treated as case II according to equation: $M_t/M_\infty = k_0 t/C_0 d$, where $C_0$ is the equilibrium concentration of penetrating agent, $d$ is the thickness of the polymer block and $k_0$ is defined as relaxation constant of polymer chains. In the case II model, gel is formed after solvent intrudes into polymer, which is separated from glassy part of the polymer by well-defined boundary of constant thickness. This boundary shifts by constant rate into the polymer [4].

In completely cross-linked systems there is no releasing of polymer chains into solvent but one can assume only swelling with formation of gel. Gel formation is accompanied by relaxation of polymer chains which is characterised by rate constant $k_0$ which might be used for characterisation of different types of polymers based on their swelling in solvents. This can be monitored by fluorescence spectroscopy because fluorescence probe can diffuse into solvent if it is not bound to polymer.

Penetration of solvent into polymers was investigated by different techniques. The simplest method is gravimetric, by which weights before and after solvent exposure are compared. ESR was employed to monitor penetration of solvents into poly(methyl methacrylate) (PMMA) latex particles [8]. Penetration of naphthalene molecules into PMMA latex particles stabilised by polyisobutylene was studied by time-resolved fluorescence spectrometry under $T_g$ [9]. The real-time non-destructive fluorescence technique for monitoring of diffusion of small molecules into polymer films has recently been developed [10–13]. This technique is based on detection of fluorescence of excited molecules desorbed from polymer film into solvent, in which the film is placed. In similar way the real-time monitoring of fluorescence probes was employed for dissolution of latex films based on steady-state fluorescence technique [14].

In this paper we describe novel approach in monitoring of swelling of interpenetrating network (IPN) using steady-state fluorescence technique. Real-time fluorescence technique was employed for monitoring excimer formation of DiPyM in toluene, which was released from IPN at swelling. 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-butanedioldimethacrylate concentrations in the original IPN preparations. The synthesis, thermal and optical properties, and dynamic-mechanical behaviour of IPN composed of PE/P(S-*co*-BMA)) have been previously reported [15,16]. 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 used this IPN for spectral characterisation of new attached fluorescent probe based on pyrene [17].

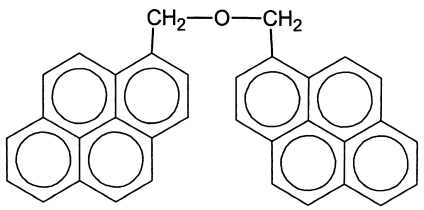
## 2. Experimental part

### 2.1. Materials

The structure of fluorescence probe used in this study is shown in Scheme 1. *Di(1-pyrenylmethyl)ether* (DiPyM) was prepared from chloromethyl-1-pyrene and 1-pyrenemethanol (Aldrich-Chemie, Steinheim, FRG) under phase-transfer condition following standard synthetic procedure [4].

The monomers used for IPN preparation were purified before use. The inhibitor of polymerisation was removed from butyl methacrylate (Merck, Schuchardt, Germany, 99%) and styrene (Chemapol, Prague, 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. 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) was used as received.

Low density polyethylene (Bralen 2-19, MFI 10 g/min, Slovnaft, Bratislava, Slovakia) was the main component in the IPN. It was labelled by DiPyM probe in two ways. In one case the DiPyM was doped to IPN by dissolving it in the initial reaction mixture consisting of PE, BMA and S. Concentration of doped probes were $10^{-4}$ or $10^{-3}$ mol kg$^{-1}$ calculated on mass of IPN. The 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 $1.9 \times 10^{-2}$ 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 and put in the oven. The reaction




Scheme 1.

was carried out at 110 °C for 5 h, followed by 1 h at 160 °C. The thickness of the IPN block was ca. 2 mm.

In second case IPN, the DiPyM label was infused into polymer block by allowing it to penetrate from toluene solution ($3 \times 10^{-4}$ mol dm$^{-3}$) at room temperature for 24 h into IPN prepared by standard procedure [15,16]. The IPN was then dried in oven at 100 °C under vacuum over 8 h. The concentration of probe in dry IPN was determined by UV spectroscopy using extinction coefficient for 1-pyrene-methanol in IPN, which had the approximate value 1.3–$1.9 \times 10^{-4}$ mol kg$^{-1}$.

Anthracene, used as fluorescence standard, was zone refined (Lachema, Brno, CR). Analytical grade toluene (Lachema, Brno, CR) was distilled and dried over molecular sieve before using. Cyclohexane was UV spectroscopy grade purity.

### 2.2. Technique

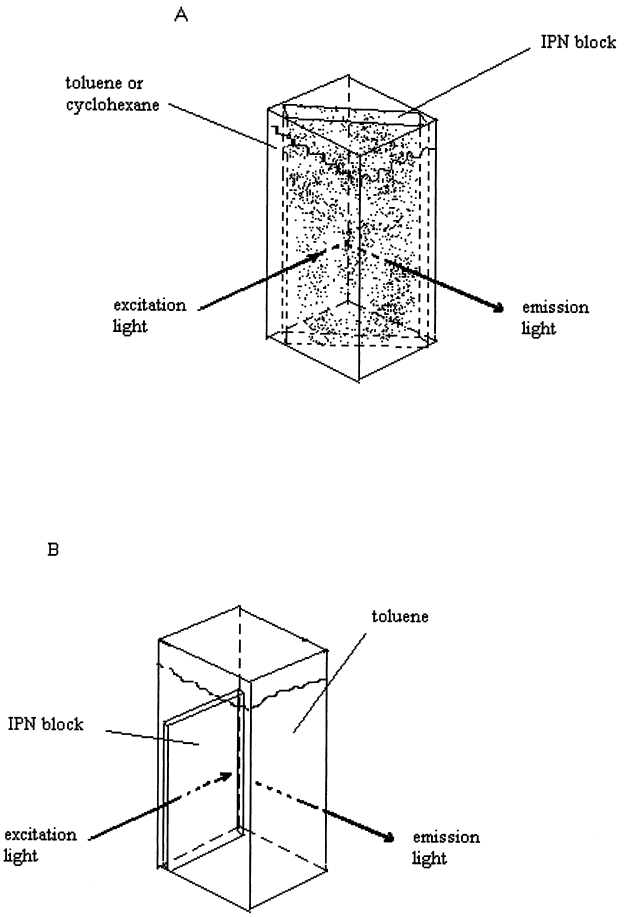
Absorption spectra were taken on a M-40 UV-VIS (C. Zeiss, Jena, Germany). Steady-state emission spectra were recorded on a Perkin–Elmer MPF-4 spectrofluorimeter (Perkin–Elmer, Norfolk, CT, USA), which was connected through interface and A/D converter to a microcomputer [18] for data collection, processing and plotting on an XY 4110 plotter (Laboratorní přístroje, Prague, CR). Emission of solutions was measured at right angle in a 1 × 1 cm cell. Emission of polymer films was measured in front-face arrangement to the solid sample holder. The emission spectra of swelled IPN blocks with doped or penetrated DiPyM were measured using a front-face arrangement in crossed position in a 1 × 1 cm cuvette at 40 °C according to Scheme 2(a).

Real-time monitoring of excimer emission of extracted DiPyM was measured at Perkin–Elmer MPF-4 spectrofluorimeter according to Scheme 2(b) with IPN block in position outside the excitation beam.

The quantum yield of polymer films was determined using anthracene as standard and assuming its low sensitivity to the medium. 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. The quantum yields in solution and in film were determined according to relation (1) [19]

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

where $\Phi_F^S$ 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 $\Phi_F^S$ for anthracene was set at 1. Integrals $\int_0^\infty I_F(\nu)d\nu$ and $\int_0^\infty I_F^S(\nu)d\nu$ are the areas under emission curves of the probe and standard, respectively, $A$ and $A^S$ are absorptions of the probe and standard at the excitation wavelength. Anthracene was excited at $\lambda_{ex} = 355–375$ nm, depending on the medium.




Scheme 2.

Fluorescence lifetime measurements were performed on a LIF 200 instrument (Lasertechnik Ltd, Berlin, Germany), which operates as a stroboscope. The excitation source was a 100 kW pulsed nitrogen laser (≈20 Hz, λ = 337 nm) with pulse duration of less than 0.5 ns. Emission in right-angle (cuvette) or front-face (polymer films or blocks) arrangement was selected by the use of cut-off filters transmitting the radiation with wavelength higher then 353 nm and detected by a photodiode. The output signal of photodiode was amplified in Box Car Integrator and the signal was then transferred to a microcomputer or PC. In the case of transferring of output signal to a microcomputer, a home-made program was used [20]. The quality of fitting was characterised by the standard deviation. In the case of transferring the data to a PC, a program of J. Snyder based on Ref. [21] was used in combination with a graphic program, Origin version 5.0 (Microsoft). Decay curves were evaluated by a simple phase-plain method when fluorescence lifetimes were similar to instrument response or up to 20 times larger [22]. When the fluorescence lifetimes are larger then 20 × the half-width of the nitrogen laser (0.5 ns), simple linear least-square fits of the data without deconvolution were applied to mono- and biexponential

functions [23]. 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 and $n$ is the number of measurements, 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 solvent swelling of IPN blocks were performed in the presence of air.

## 3. Results and discussion

### 3.1. Absorption and emission characteristics in dry IPN

The absorption spectra of DiPyM in toluene and dry IPN are similar to that which has been observed in other polymer matrices and show the well resolved longest wavelength band at 316, 330, 347 nm (Fig. 1; Table 1). The position of maximums of DiPyM in IPN is also similar as in other polymer matrices [4]. The position of maximums given by the penetrated probe compared with probe added at preparation is slightly shifted to longer wavelength (Table 1). The absorption spectrum of DiPyM in toluene is similar to that in other solvents [3]. The shape of the spectrum is similar to that of unsubstituted or monosubstituted pyrene, indicating no interaction between pyrene rings in DiPyM. The absorption edge of DiPyM in IPN is shifted to longer wavelength (red shift), which is probably due to the medium.

Similarly, the emission spectra of DiPyM in dry IPN is the same as in other polymer matrices with several resolved vibrational bands at 378, 388 (389), 398 (401) nm. Depending on the medium, these bands result from monomeric probe fluorescence (Fig. 1; Table 1). There

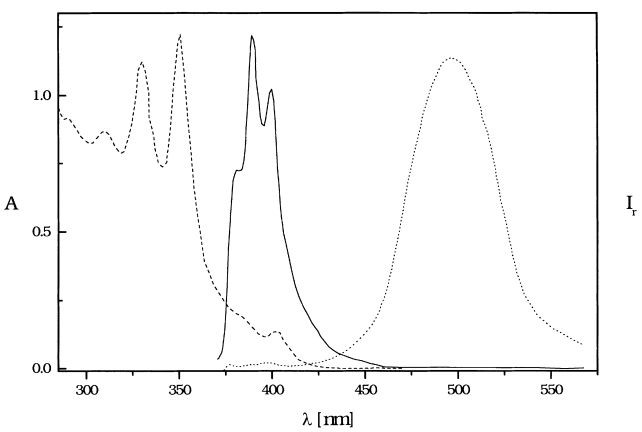



Fig. 1. Absorption (dashed line) and emission spectrum (full line) of DiPyM doped in preparation in dry IPN (0.5 mol% BDDM) with concentration of probe $10^{-3}$ mol kg$^{-1}$, $\lambda_{ex} = 353$ nm and emission spectrum of DiPyM (dotted line) in toluene with concentration of probe $10^{-5}$ mol dm$^{-3}$, $\lambda_{ex} = 347$ nm.

was no difference between the fluorescence spectra of the DiPyM regardless whether it was penetrated into the prepared IPN or added to the mixture of PE dissolved in monomers at time of IPN preparation. Contrary to its behaviour in polymer matrices, DiPyM exhibits a lone, broad excimer emission at 495 nm in toluene or cyclohexane. No vibrational structure at 495 nm in liquid toluene, cyclohexane or other liquid media has previously been observed [1,2,4] (Fig. 1).

Quantum yield of fluorescence relative to anthracene is slightly higher for penetrated probe into IPN than for probe incorporated at preparation (Table 1). This effect is evident for IPN with 0.5 and 3 mol% of BDDM. The lower quantum yield of fluorescence of probe doped at preparation was also observed in our previous paper [17]. This decrease of quantum yield might be due to modification of the pyrene chromophore by radicals generated during IPN preparation. The absence of the vibrational band in the fluorescence spectrum at 378 nm indicates some modification of pyrene chromophore. Grafting of PE with pyrene implies some ability toward radical reaction [24]. Generally, there are several potential sites for radical reaction on pyrene during IPN preparation. In contrast, the quantum yield of fluorescence for penetrated probe is comparable with those in other polymer matrices, since no radicals are involved in preparation.

The lifetime of fluorescence DiPyM in dry solid polymer matrices is longer than 100 ns in IPN. In these matrices the bichromophoric probe forms no excimer, consequently the emission is due to the fluorescence of the monomeric form, which decays in a monoexponential manner (Table 1). Generally, the fluorescence lifetime of monosubstituted derivatives (such as our probe DiPyM) is shorter than that of pyrene under the same condition. The longest lifetime is exhibited by unsubstituted pyrene in well-deaerated cyclohexane (450 ns) [25]. Shortening of lifetime of DiPyM might be due to the fact that there are residues of vinyl monomers in the IPN block, which are difficult to remove. Moreover, all lifetime measurements with IPN block were performed on air. In liquid media, where DiPyM forms excimers, the lifetime of excimer emission is around 30–60 ns.

### 3.2. Monitoring of swelling of IPN by steady-state fluorescence technique

Diffusion coefficients of toluene or cyclohexane in complex polymer system such as IPN are not known. However, the value of diffusion coefficient can be roughly estimated from swelling behaviour of the polymer in the given solvent. The ratio of mass of absorbed solvent and sample at equilibrium conditions (40 °C) was determined by gravimetry for swelling of IPN in toluene and cyclohexane according to: $\alpha = m_s/m_{IPN}$, where $m_s$ is weight of absorbed solution in IPN and $m_{IPN}$ is weight of original IPN sample. The data in Table 2 and data from Fig. 2 clearly indicate that

Table 1
Absorption and emission characteristics of DiPyM in IPN blocks

| BDDM (mol%) | Processing[a] | $\lambda_{abs}$[b] | $\lambda_{ex}$[c] | $\lambda_{em}$[d] | $\Phi_r$[e] | $\tau$[f] (ns) |
|---|---|---|---|---|---|---|
| 0.5 | Doped | 316, 330, 347 | 353 | 389, 401 | 0.08 | 152 |
| | Penetrated | 318, 351 | 353 | 378, 388, 398 | 0.26 | 182 |
| | Swelled | – | 355 | 391, 409, 495 | – | 25 |
| 1 | Doped | 316, 330, 347 | 353 | 389, 401 | 0.23 | 191 |
| | Penetrated | 318, 351 | 353 | 378, 388, 398 | 0.26 | 227 |
| | Swelled | – | 355 | 392, 408, 495 | – | 29 |
| 3 | Doped | 317, 330, 348 | 353 | 389, 401 | 0.07 | 154 |
| | Penetrated | 318, 351 | 353 | 378, 388, 398 | 0.31 | 164 |
| | Swelled | – | 355 | 391, 408, 492 | – | 33 |
| Toluene | $10^{-5}$ mol dm$^{-3}$ | 317, 330, 347 | 347 | 495 | 1.2 | 34 |

Comparison of cross-link density, probe addition process and toluene swelling at 40 °C for 4 h.
[a] Concentration of DiPyM doped to IPN during preparation was $1 \times 10^{-4}$ mol kg$^{-1}$, averaged concentration of penetrated probe was around $1.5 \times 10^{-4}$ mol kg$^{-1}$.
[b] Longest-wavelenght absorption bands.
[c] Excitation wavelength.
[d] Wavelength of emission bands.
[e] Quantum yield relative to anthracene. The estimated error is ±20%.
[f] Fluorescence lifetime evaluated as monoexponentials without deconvolution.

solvents penetrate into the IPN with different rates depending on the density of the network. Not unexpectedly, a denser IPN network swells less than the less dense one.

Swelling of IPN by toluene and cyclohexane was performed in the heated cell of spectrofluorimeter in aerated solvent and without stirring (Scheme 2(a)). Formation of excimer emission was monitored by measurement of emission spectra during swelling time. The rate of increase of excimer emission was investigated for IPNs having different content of cross-linker and for samples in which probe was added at time of preparation or penetrated by the infusion method.

The emission spectrum of probe doped at the preparation does not change much during swelling with toluene and cyclohexane as compared with the spectrum of the dry sample (Fig. 3). In this case, weak excimer emission is observed at swelling of the IPN in toluene, only. Therefore, the ratio of excimer to monomer emission $I_e/I_m$ is low and this value does not change significantly with time (Fig. 3). No excimer at all was observed in the sample swollen in cyclohexane and which was doped at preparation. This is because cyclohexane is a weak swelling agent. Therefore, toluene, the more efficient swelling agent, was used in further experiments. The toluene extract of IPN doped with DiPyM at preparation shows a low excimer emission, confirming that the extraction of probe (DiPyM) in this case is limited. This suggests that DiPyM doped at preparation is subject to some changes during polymerisation, possibly resulting in linking to matrix, entrapment in the network or chemical change.

Table 2
Value of swelling degree $\alpha$ for toluene and cyclohexane absorbed into IPN with different network density at 40 °C

| BDDM in IPN (mol%) | $\alpha$ (toluene) | $\alpha$ (cyclohexane) |
|---|---|---|
| 0.5 | 2.2 | 1.14 |
| 1 | 1.65 | 0.9 |
| 3 | 1.32 | 0.64 |

The overall intensity of the emission during swelling steadily decreases because toluene penetrating into the IPN block contains oxygen which acts as quencher. The solvent itself influences the excited states of the molecules because the interaction between chromophore and solvents results in different energy between ground and excited state [26]. Moreover, the solvent can act as an energy sink for rapid vibrational relaxation after chromophore excitation as compared to solid-state behaviour.

Excimer emission of IPN containing DiPyM which had been penetrated by the infusion method, increased distinctly with swelling time in toluene at 40 °C (Fig. 4). The

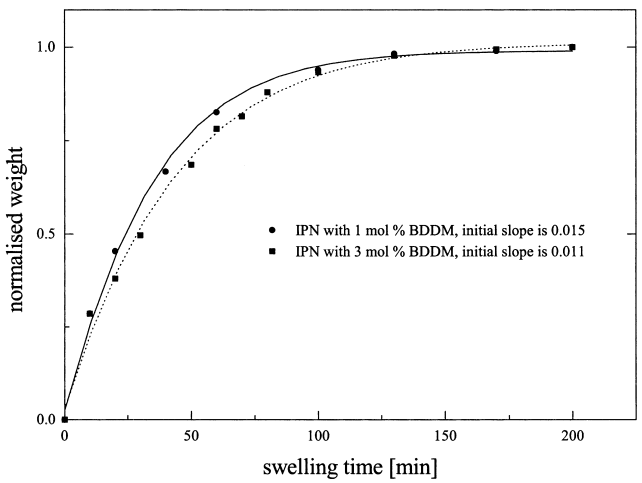



Fig. 2. Monitoring of swelling of IPN with different network density in toluene at 40 °C by gravimetry methods. IPN with 1 mol% of BDDM (full line) and with 3 mol% of BDDM (dotted line).

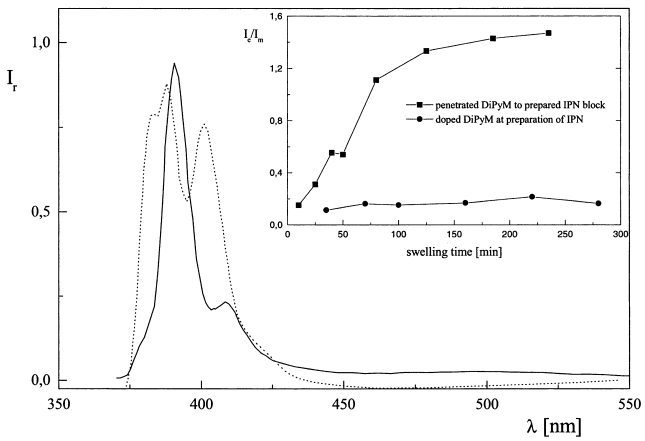



Fig. 3. Emission spectra of DiPyM doped at IPN preparation (1 mol% BDDM) and swelled 90 min in toluene (full line) and 210 min in cyclohexane (dotted line) at 40 °C. $I_e/I_m$ ratio for doped ($10^{-4}$ mol kg$^{-1}$) and penetrated (approximately $1.5 \times 10^{-4}$ mol kg$^{-1}$) DiPyM in IPN (0.5 mol% BDDM) in dependence on swelling time. IPN was swelled in toluene at 40 °C.

experiment was performed according to Scheme 2(a). In this case the excimer emission originates exclusively from IPN block. As seen in Fig. 3, the ratio $I_e/I_m$ increases over 1 for penetrated DiPyM as compared with the $I_e/I_m$ ratio observed with DiPyM doped at preparation. The latter shows small change under the same conditions. Clearly the DiPyM probe penetrated into IPN has a higher mobility. No difference, however, was observed for the swelling rate of samples for which the probe was introduced by either method. This is based on a plot of increase in $I_e/I_m$ on time by monitoring the excimer emission for IPNs having different cross-linking

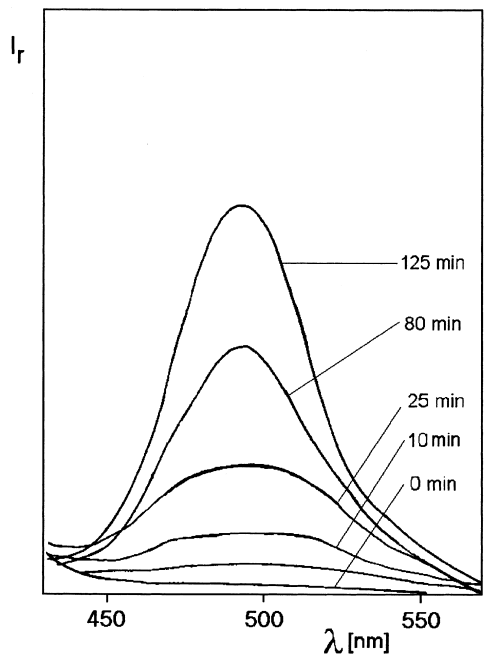



Fig. 4. Dependence of excimer emission at $\lambda_{em} = 495$ nm of penetrated DiPyM in IPN on swelling time, excitation wavelength $\lambda_{ex} = 355$ nm. IPN was swelled in toluene at 40 °C.

density. Weighing clearly shows the difference in swelling rate ($\alpha = 2.2$ for 0.5 mol% BDDM and $\alpha = 1.32$ for 3 mol% BDDM). Molecules of DiPyM are sufficiently large that they require a relatively large volume for free rotational movement, which is necessary in order to observe excimer emission. In the solid state (bulk IPN block) all rotational movements are frozen, therefore, no excimer is observed. After swelling of IPN, this large probe does not experience a big difference between networks cross-linked with 0.5 and 3 mol% of BDDM. The solvent swells the IPN block very quickly, thus allowing excimer to form immediately. However, the probe feels the difference in the network density during solvent extraction.

### *3.3. Monitoring of swelling of IPN by real-time fluorescence technique*

The rate of extraction of probe from IPN followed by formation of excimer in solvent offered more clear dependence on the cross-link density of IPN (Fig. 5). The excimer emission at 495 nm was followed with swelling time in toluene. Excitation was at 355 nm and the arrangement shown in Scheme 2(b) was used in order to optimise excimer emission compared to that generated by the monomeric form. From Fig. 5 it follows that the maximum of excimer emission for IPN with 1 mol% BDDM was reached after 80 min, but for IPN with 3 mol% BDDM, the maximum occurred approximately after 110 min. In comparison of the gravimetric procedure, these times to achieve equilibrium are shorter and larger difference is observed for different cross-link densities. By gravimetry, the time needed for swelling of IPN with 1 mol% BDDM, is 120 min while for 3 mol% BDDM it is 145 min (Fig. 2). This means that doped or penetrated

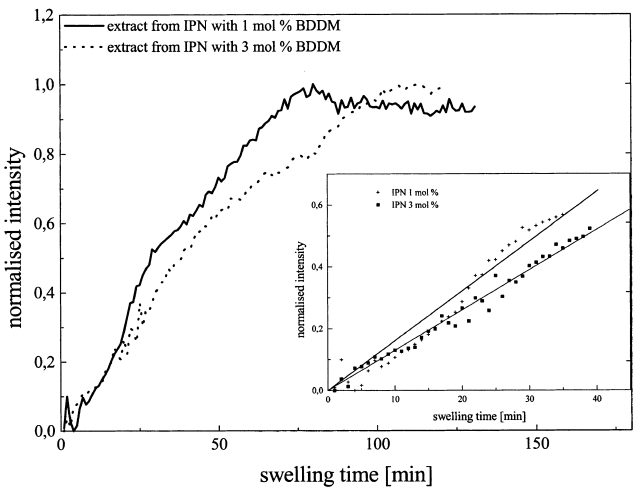



Fig. 5. Comparison of rate of extraction of DiPyM from IPN with different cross-linking density measured by formation of excimer emission in toluene and comparison of the linear portion of excimer increase intensity with computations using equation $I_t = k_0 t/C_0 d$. Constants $k_0$ are obtained from the slopes of the plots for the excimer intensity of DiPyM extracted from IPN blocks.

DiPyM in IPN is located in sites with larger free volume. These are swollen faster with toluene and allow the probe to be more quickly extracted. In contrast to this, extended Soxlet extraction of the IPN could not remove all of the DiPyM, which had previously penetrated the sample. This indicates some flexibility of the network, however, there must be sites which can entrap the DiPyM, although originally it was penetrated from toluene into IPN at laboratory temperature.

The relaxation constant $k_0$ can be evaluated based on curves of formation of excimer emission intensity of DiPyM with swelling time in toluene. In case II, outdiffusion kinetics, $k_0$ is the rate constant for the relaxing of segments during swelling and consequently releasing of molecules of DiPyM from swollen IPN. One can say that $k_0$ characterises the IPN based on its cross-link density. In the Fick's law equation, the ratio of masses $M_t/M_\infty$ can be substituted by ratio of intensities $I_t/I_\infty$and taking $I_\infty = 1$, the equation takes the form $I_t = k_0 t/C_0 d$. The slopes were calculated for the initial part of the dependence of the excimer emission of DiPyM on time (Fig. 5) and used to calculate $k_0$ (Table 3). These values indicate that the releasing of the DiPyM is slower for more dense network (3 mol% BDDM) than for less dense network (1 mol% BDDM).

Drying of the swelled IPN samples for 24 h in toluene as monitored by decrease in weight (Fig. 6) occurs at the same rate for IPN with different cross-link densities. This means that the rate of evaporation of toluene at laboratory temperature is rate determining and not the rate of toluene releasing from the IPN. It takes about 450 min of ambient drying for equilibrium to be reached and for the weight of the sample to remain unchanged. This time is more or less independent on the size of sample. Under these conditions the solvent, however, is not removed completely from IPN.

The course of swelling or solvent removal (drying) can be followed by change of fluorescence lifetime of the probe (DiPyM), since the swelling agent (toluene) transports quencher oxygen as well. The change of lifetime of DiPyM is an abrupt decrease from 200 to about 20 ns upon pouring of toluene into cell with dry IPN. It was therefore difficult to follow the course of penetration of toluene into IPN. This effect was observed for IPN samples with different cross-links densities. It was much easier to monitor the lifetime of DiPyM during drying. The lifetime increased from about 23 to about 170 ns after about 168 h. The original value of lifetime above 200 ns was, however, not obtained. Further

Table 3
Variation of relaxation constant $k_0$ with cross-link density of IPN swollen by toluene

| IPN | $k_0 \times 10^{-4}$ (mg cm$^{-2}$ min$^{-1}$) | $d$ (cm) |
|---|---|---|
| 1 mol% BDDM | 2.26 | 0.21 |
| 3 mol% BDDM | 1.78 | 0.205 |

Values of $k_0$ obtained by fitting equation $I_t = k_0 t/C_0 d$ to the data in Fig. 5.

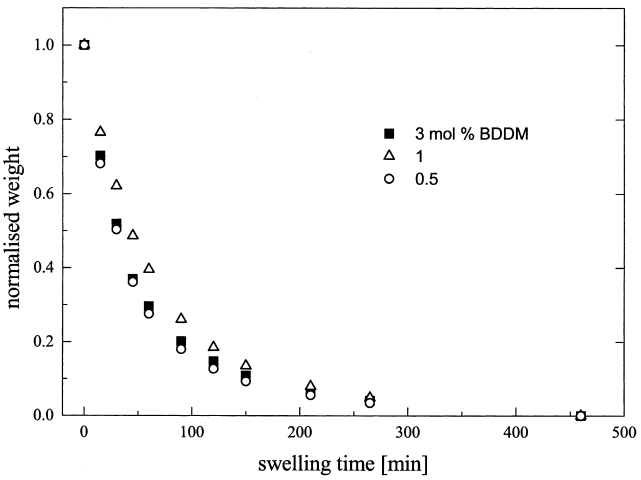



Fig. 6. The rate of drying of IPN with different density after swelling in toluene for 24 h.

increase in lifetime would require more rigorous drying at higher temperature and under vacuum. Again, the changes among IPNs with different cross-link densities were not observed because the lifetimes of DiPyM in different IPN samples had a wide margin of error.

## 4. Conclusions

Monitoring of swelling of IPN in toluene and cyclohexane by fluorescence spectroscopy revealed that fluorescence probe, DiPyM, doped at preparation of IPN yields no excimer emission. This behaviour is due to chemical or physical reasons. Some of DiPyM may be chemically bound to IPN (grafted to PE or copolymer). This is mainly valid for samples in which DiPyM is introduced at preparation. Some of the probe may also become physically entrapped at sites of entanglements during the course of formation of copolymer (S-*co*-BMA) and of cross-links in the IPN. It was not possible to completely extract the probe from the IPN, although it does not contain functional group for binding.

Emission from IPNs having different cross-link densities was achieved by application of real-time fluorescence technique employing probe penetrated into prepared IPN blocks. In this case the rate of releasing of DiPyM from IPN is dependent on the rate $k_0$ of relaxation of polymer chains at swelling. The $k_0$ is equal $2.26 \times 10^{-4}$ mg cm$^{-2}$ min$^{-1}$ for network with 1 mol% BDDM and $1.78 \times 10^{-4}$ mg cm$^{-2}$ min$^{-1}$ for network with 3 mol% BDDM.

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