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Journal of Photochemistry and Photobiology A: Chemistry 154 (2003) 279–288

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Characterization of interpenetrating polymer-like network based on polyethylene/poly(styrene-co-butylmethacrylate) (PE/P(S-co-BMA)) by non-radiative energy transfer

Martin Danko, Pavol Hrdlovič*, Eberhard Borsig

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

Received 8 August 2002; accepted 27 August 2002

Abstract

Preparation of labeled interpenetrating polymer-like network (IPN) composed of polyethylene and copolymer styrene and butylmethacrylate with polymerizable fluorescence probes based on phenanthrene and anthracene was described. This pair of fluorescence probes, namely (phenathrene-9-yl)methyl methacrylate and (anthracene-9-yl)methyl methacrylate, was used to explore the non-radiative energy transfer in this special polymer blend. It was demonstrated that the energy transfer between phenanthrene moiety attached to copolymer part of IPN and anthracene moiety attached to PE part of IPN occurred in rather limited extent due to micro-heterogeneous structure of this polymer blend. Fluorescence experiments with dyes attached solely to the copolymer S-BMA part of IPN indicated that these dyes were concentrated in this part of IPN.

Keywords: Interpenetrating polymer-like network; Non-radiative energy transfer; Fluorescence probes; Phenanthrene; Anthracene

1. Introduction

Non-radiative energy transfer (NRET) has proven to be a useful and general method for studying miscibility in polymer blends and it has been pioneered by Morawetz [1,2]. In this type of experiment the extent of the energy transfer provided a measure of the extent of miscibility between the two polymers. Application of NRET technique was used for characterization of structure of core polymer micelles [3] or for determining of the interface thickness of micro-domains in the polymer blends [4].

Successful labeling of the polyolefins creates the possibility of using NRET experiments to study a variety of interesting properties of these type of polymers and their blends [5,6]. They anticipate for semi-crystalline polyolefins that dyes would be confined to the amorphous domains such that as the degree of crystalline fraction increased, the local concentration of dyes in the amorphous domains would increase accordingly.

There are few reports on the blend of conventional engineering polyolefins like polypropylene or UHMW PE with polysilanes, which have interesting electronic and optical properties [7]. Polysilanes exhibit strong fluorescence, which can be utilizing for energy transfer between chromophores. Recently, Torkelson and coworkers [8] show application of NRET technique for the study of the Fickian diffusion of small molecules in rubbery polymer matrices. They used pyrene as donor, which was attached to poly(isobutyl methacrylate) or polyethyl methacrylate and acceptor decacyclene or 9,10-bisphenyl-ethynyl anthracene, respectively.

A most useful pair of dyes for direct NRET experiments are phenanthrene (Phe) as donor of energy, which can be excited selectively and the energy transfer from the excited Phe* to anthracene (Ant) as acceptor energy can be monitored by steady state or time-resolved fluorescence techniques. For probes used for NRET in polymers, it is necessary to establish appropriate limiting conditions, which are full characterization of polymer matrix, to determine the spectroscopic properties of dyes in the polymer and random distribution of dyes in the polymer matrix. Aggregation of dyes depends sensitively on the choice of dye and on the nature of the functional groups used to attach the dye to the polymer backbone [9]. Energy transfer for this

* Corresponding author. Tel.: +421-2-5477-7405; fax: +421-2-5477-5923.
E-mail addresses: upoldan@savba.sk (M. Danko), upolhrdl@savba.sk (P. Hrdlovič), upolebor@savba.sk (E. Borsig).

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PII: S1010-6030(02)00323-4

pair of probes in polymer film occurs by a dipole coupling mechanism and leads to non-exponential fluorescence decay curves. For a system with uniformly distributed donors and acceptors in three dimensions, the donor fluorescence intensity decay $I_d(t)$ should follow the Förster equation (Eq. (1)), where τ_0 is the donor fluorescence lifetime in the absence of acceptor and the factor P is proportional to the acceptor (quencher) concentration $[Q]$ (Eq. (2)) [6].

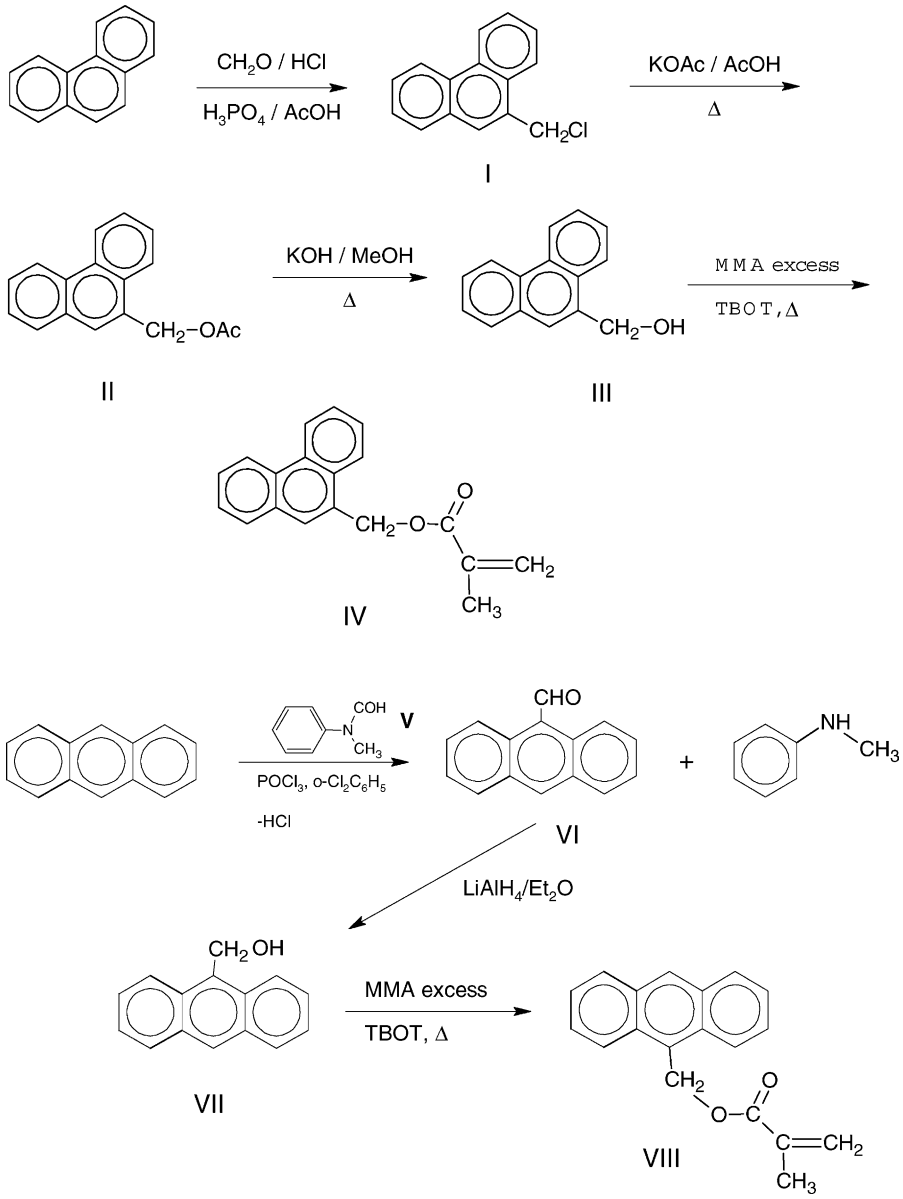
$$I(t) = A \exp\left[-\frac{t}{\tau_0} P \left(\frac{t}{\tau_0}\right)^{0.5}\right] \quad (1)$$

$$P = \gamma \frac{4\pi^{3/2}}{3000} N R_0 [Q] \quad (2)$$

In Eq. (2), γ is an orientation factor, N the Avogadro's number and R_0 is the critical (Förster) radius for energy transfer. The criterion for Förster-type energy transfer is a spectral overlap between donor emission and acceptor absorption [10]. The Perrin equation (Eq. (3)) is based on simplified model of fluorescence quenching among immobile fluorophores and quenchers [6]. In this model, a quencher is deemed to quench an excited chromophore instantaneously if the quencher Q is within a sphere of radius R_s centered on the chromophore and to be ineffective at quenching if their separation is larger than R_s. In Eq. (3), F is the fluorescence intensity in the presence of quenchers and F_0 is the fluorescence intensity in the absence of quencher $[Q] = 0$.

$$\ln \frac{F_0}{F} = \frac{4}{3} \pi R_s^3 [Q] \quad (3)$$

In our experiments, fluorescence intensities were calculated from the integrated normalized steady-state fluorescence of



Scheme 1.

donor (Eq. (4)).

$$F = \int_0^\infty I(\nu)\,\mathrm{d}\nu \tag{4}$$

In this paper we described NRET from Phe to Ant in special polymer blend as interpenetrating polymer-like network (IPN) based on polyethylene/poly(styrene-co-butylmethacrylate) (PE/P(S-co-BMA)). This IPN is a two-phase polymer blend consist of PE continuous phase in which P(S-co-BMA) copolymer domain is randomly distributed [11]. Spectral characteristic of pyrene type probes in this complex polymer blend was investigated earlier [12]. In our experiments, we attached probes via ester groups of methyl methacrylate by terpolymerization of dyes (phenathrene-9-yl)methyl methacrylate (Scheme 1, **IV**) and (anthracene-9-yl)methyl methacrylate (Scheme 1, **VII**) to a copolymer phase of IPN and by reaction of attached maleine anhydride to PE phase with 9-anthracenemethanol. We attempted to determine the extent of the third, interpenetrated, phase, which exists at the boundaries of PE phase and S-co-BMA phase in this system. These results are compared with energy transfer from doped unsubstituted phenanthrene to unsubstituted anthracene in IPN system. This is the first investigation employing NRET technique for characterization of the micro-structure of this special type of polymer blend.

2. Experimental

The structures and ways of preparation of the fluorescent probes used in this paper are shown in Scheme 1. The synthesis of the derivatives (phenanthrene-9-yl)methyl methacrylate (PhMMA, **IV**) and (anthracene-9-yl)methyl methacrylate (AMMA, **VIII**) were performed by reesterification reaction of methyl methacrylate with the subsequent alcohol using tetrabutyl orthotitanate (TBOT) as reesterification catalyst [12,13]. Modification of LDPE with maleine anhydride (MAN) was performed in xylene using dicumylperoxide (DCP) according to the described procedure [14]. Labeling of LDPE with anthracene was performed by the reaction of attached maleine anhydride to LDPE with 9-anthracenemethanol in xylene solution. Labeling of IPNs were performed by terpolymerization of (phenanthrene-9-yl)methyl methacrylate or (anthracene-9-yl)methyl methacrylate with styrene and butyl methacrylate for preparation of IPNs [12].

2.1. Preparation of probes

2.1.1. 9-Chlormethylphenanthrene [15] (*I*)

Mixture of phenanthrene (4 g, 0.0225 mol), paraformaldehyde (1.24 g, 0.041 mol), glacial acetic acid (4 ml), 12 M HCl (12.5 ml) and 85% H_3PO_4 (1.9 ml) was vigorously stirred in a 50 ml flask fitted with reflux condenser and kept on a water bath at 85 °C for 40 h. Then the mixture was poured onto crushed ice and extracted with ether (3 × 100 ml). The combined organic layers were washed with H_2O until neutral reaction, dried over Na_2SO_4 and the solvent was removed in vacuo to leave a crude dark oil of product (4.96 g, 97%) which was used without further purification in the subsequent step.

2.1.2. (Phenanthrene-9-yl)methyl acetate [15] (*II*)

Crude 9-chlormethylphenanthrene (2 g, 0.008 mol) in glacial acetic acid (4.2 ml) was refluxed 7 h with potassium acetate (1.6 g). Then the mixture was poured on ice and extracted with ether (2 × 50 ml). The organic extract was washed with saturated solution of $NaHSO_4$ (4 × 20 ml) and H_2O (2 × 20 ml) until neutral, dried over Na_2SO_4 and the solvent was removed in vacuo to leave a dark viscous residue (1.75 g). TLC chromatography (eluent benzene) showed unreacted phenanthrene, product and side products. The oily product (1.07 g) was obtained by chromatography on silica gel column (180 g, eluent ligroin:ethyl acetate, 20:1). Crystallization from *n*-hexane and *n*-butanol yielded 0.6 g of pure product with m.p. 69–74 °C (Ref. [15], 79–80 °C). The purity of product was proved by HPLC chromatography.

2.1.3. 9-Phenanthrylmethanol [15] (*III*)

A mixture of 9-phenanthrylmethyl acetate (0.224 g, 0.89 mmol) and KOH (0.171 g, 3 mmol) in MeOH (2 ml) and H_2O (0.3 ml) was refluxed in flask under condenser for 6 h. Then the reaction mixture was poured into 10 ml of H_2O and extracted with ether (3 × 20 ml). The combined etheral extracts was washed with water (2 × 20 ml) and dried over Na_2SO_4. After evaporation of ether, the solid product (0.18 g, 97%) was obtained. Crystallization from benzene yielded white needles of alcohol (0.136 g), m.p. 128–143 °C (Ref. [15], 150.5–151 °C). The purity of product was proved by HPLC and gas chromatography.

^{1}H NMR ($CDCl_3$) δ: 1.56 (s, 1H, OH), 5.2 (d, 2H, CH_2–O), 7.57–8.76 (m, 9H, phenanthrene). FTIR (KBr): ν(OH) 3196 cm^{-1}, ν(phenanthrene) 725 cm^{-1}, MS (M^+): 208, 189, 179, 151, 126, 74.

2.1.4. (Phenanthrene-9-yl)methyl methacrylate (PhMMA) (*IV*)

Refluxing solution of 9-phenanthrylmethanol (0.4 g, 1.92 mmol) and freshly distilled methyl methacrylate (30 ml) with polymerization inhibitor IONOL AO4K (0.012 g) was mixed with three drops of tetrabutyl orthotitanate (TBOT) as reesterification catalyst. Reaction was carried out under argon atmosphere of 6 h. A small amount of polymethyl methacrylate precipitated on cooling with addition of 300 ml of methanol. After filtration, the solvent was removed under reduced pressure. The crude product was obtained by chromatography on silica gel column (90 g, eluent ligroin:ethyl acetate, 20:1). White crystals of monomer (0.37 g, 70%) with m.p. 63–73 °C was obtained after crystallization from ligroin. The purity of product was proved by HPLC chromatography.

^{1}H NMR ($CDCl_3$) δ: 1.98 (m, 3H, CH_3), 5.58 (m, 1H, =CH_2 *cis*), 5.69 (s, 2H, –CH_2–), 6.15 (m, 1H, =CH_2 *trans*), 7.58–8.76 (m, 9H, phenanthrene). FTIR (KBr): ν(C=O) 1718 cm^{-1}, ν(C–O–C) 1185 cm^{-1}, ν(phenanthrene) 720 cm^{-1}. UV spectrum (MeOH) (λ [nm] ($\log \varepsilon$)): 253 (4.7), 275 (3.5), 285 (3.5), 295 (3.9).

2.1.5. *N-methylformanilide [16]* (***V***)

Mixture of *N*-methylaniline (32.1 g, 0.3 mol), formic acid (30 g, 0.65 mol) and 180 ml of toluene was slowly distilled through a 40 cm column and condenser. Temperature of distillation vapors was 84–85 °C, while azeotropic mixture of toluene/water was distilled. When 78 ml of azeotropic mixture was distilled off, temperature was increased to 104–110 °C and 105 ml of toluene was distilled off. Rest of the solution was transferred to Claisen distillation flask and distilled under reduce pressure. First fraction (15 ml) was traces of toluene, second fraction was product with b.p. 101–104 °C/4 mm (Ref. [16], 114–121 °C/8 mm). Weight of product was 35.91 g (89%) and temperature of solidifying liquid was 12 °C.

2.1.6. *9-Anthracenealdehyd [17]* (***VI***)

To a mixture of *N*-methylformanilide (14.87 g, 0.115 mol) and *o*-dichlorobenzene (8.9 ml) in 250 ml three-necked flask equipped with mechanical stirrer and reflux condenser was added in portion $POCl_3$ (15.6 g, 0.1 mol). After addition of anthracene (10 g, 0.056 mol), the reaction mixture was heated on the oil bath to 96 °C under stirring over a period of 2 h. A solution of sodium acetate (62.2 g) in 111 ml of H_2O was added to a cooled mixture and the *o*-dichlorobenzene and amine was rapidly distilled with steam. The solid residue was decanted through Büchner funnel and washed by decantation with 6 M HCl (2 × 50 ml) and H_2O (700 ml). The crude residue was crystallized from hot glacial acetic acid (30 ml), filtered and washed on the filter with MeOH (35 ml). The yield was 9.27–9.77 g (80–84%) bright yellow crystals of aldehyde with m.p. 97–99 °C (Ref. [17], 104.5–105 °C). FTIR (KBr): ν(CHO) 1670 cm^{-1}, ν(anthracene) 735 cm^{-1}.

2.1.7. *9-Anthracenemethanol [18]* (***VII***)

Suspension of $LiAlH_4$ (3.18 g, 0.084 mol) in diethylether (250 ml) was refluxed through Soxhlet extraction apparatus where 9-anthracenealdehyd (8.73 g, 0.042 mol) was placed. Reaction mixture was refluxed with vigorous stirring for 7 h, during which the aldehyde went into solution. The remaining $LiAlH_4$ was decomposed by addition of ethyl acetate (100 ml) followed by 100 ml of water and solution of 3 M HCl (150 ml) to decompose the complex. After extraction with ether the organic layer was dried and solvent was evaporated. Crude yellow crystals of alcohol (6.74 g, 77%) were recrystallized from ethyl acetate (5×) to give 4.05 g (47%) of pure alcohol with m.p. 161–162.5 °C (Ref. [19], 155–157 °C).

^{1}H NMR ($CDCl_3$) δ: 1.56 (s, 1H, OH), 5.67 (s, 2H, CH_2–O), 7.46–7.59 (m, 4H, H-2,3,6,7 anthracene), 8.02–8.04 (m, 2H, H-4,5 anthracene), 8.40–8.43 (m, 2H, H-1,8 anthracene), 8.47 (s, 1H, H-10 anthracene). FTIR (KBr): ν(OH) 3415 cm^{-1}, ν(anthracene) 735 cm^{-1}.

2.1.8. *(Anthracene-9-yl)methyl methacrylate (AMMA)* (***VIII***)

The solution of 9-anthracenemethanol (1 g, 4.8 mmol) in MMA was refluxed 4 h in case of preparation of probe **IV**. The crude oily product after precipitation of polymer and evaporation of solvent was analyzed by HPLC chromatography. Crystalline product (0.66 g, 50%, m.p. 83–84 °C (Ref. [20], 83–84 °C)) was obtained after chromatography on silica gel column (200 g, eluent ligroin:ethyl acetate, 10:1) and recrystallization from ligroin.

^{1}H NMR ($CDCl_3$) δ: 1.92 (s, 3H, CH_3), 5.5–5.52 (m, 1H, =CH_2 *cis*), 6.06 (s, 1H, =CH_2 *trans*), 6.22 (s, 2H, –CH_2–O), 7.47–7.6 (m, 4H, H-2,3,6,7 anthracene), 8.02–8.05 (d, 2H, H-4,5 anthracene), 8.36–8.39 (d, 2H, H-1,8 anthracene), 8.51 (s, 1H, H-10 anthracene). FTIR (KBr): ν(C=O) 1710 cm^{-1}, ν(C–O–C) 1758 cm^{-1}, ν(anthracene) 735 cm^{-1}. UV spectrum (MeOH) (λ [nm] (log ε)): 254 (5.2), 349 (3.8), 363 (3.9), 386 (3.9).

2.2. *Modification of LDPE*

Solution of LDPE (Bralen 2-19, MFI 2 g/10 min, Slovnaft SA, Bratislava, SR) (20 g) and MAN (Merck, Schuchardt, Germany, >99%) (0.1 mol) in dry xylene (200 ml) was mixed in portion to a solution of DCP (Merck, Schuchardt, Germany, >98%) in xylene. Reaction mixture was refluxed at 135 °C for 90 min under stirring and argon atmosphere. Concentration of DCP was 1.4×10^{-3} mol dm^{-3} for solution. Then the LDPE was precipitated in dry acetone (dried with P_2O_5) and filtered. Unreacted MAN was extracted in Soxhlet apparatus with acetone for 18 h. The amount of grafted MAN was 1.11 wt.% (1.1×10^{-1} mol kg^{-1}) and was determined by modified titration method [21].

For labeling of LDPE with anthracene, organic reaction of anhydride group with alcohol producing ester group was utilized. Solution of 1 g modified LDPE, 2.3 mg (1×10^{-2} mol kg^{-1}), 9-anthracenemethanol (0.1 mol kg^{-1}) and catalytic amount of *para*-toluene sulfonic acid in dry xylene (100 ml) was vigorously stirred at 120 °C under argon atmosphere for 3.5 h. Modified LDPE was precipitated from hot reaction mixture with dry acetone. LDPE was reprecipitated from solution of xylene with methanol to remove unreacted alcohol. After drying in vacuo the amount of bound chromophore of anthracene was calculated from Lambert–Beer equation using UV spectroscopy. Concentration of bound anthracene ($\log \varepsilon = 3.88$ for AMMA in LDPE film at 369 nm) was 1.68×10^{-2} mol kg^{-1}.

The inhibitor of polymerization was removed from butyl methacrylate (Merck, Schuchardt, Germany, 99%) and styrene (Chemapol, Prague, CR) 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 initiator for IPN formation, 2,5-dimethyl-2,5-di-(*tert*-butylperoxy)hexane (Luperox 101) (Luperox, GmbH Germany) was used.

IPNs were prepared by dissolving LDPE and fluorescent probe (concentration of donor was 10^{-2} mol kg^{-1} and concentrations of acceptor were 1–4 $\times$ 10^{-2} 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 polymerization 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 within the confines of a glass spacer (1 mm thick) and put in the oven. The reaction was carried out at 110 °C for 5 h followed by 1 h at 160 °C. The IPN with grafted PE and terpolymer S-co-BMA-co-probe were prepared in the same way. The thickness of IPN films were about 1 mm.

2.3. 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, USA), which was connected through interface and A/D converter to a microcomputer [22] or personal computer (PC) for data collection. Emission of polymer films was measured in front-face arrangement to the solid sample holder. Integral emission intensities of donor and acceptor were calculated using Origin 5.0 graphic program (Microsoft). ^{1}H NMR spectra were taken on Bruker spectrometer with frequency 300 MHz. High pressure liquid chromatography (HPLC) was performed on the apparatus: high pressure pump HPP 4001 (Laboratorní přístroje n.e. Prague, CR), column Sepharon SGX-C 18 with diameter of pores 5 μm (Tessek Ltd., Prague, CR), UV detector LCD 2563 (254 nm, Laboratorní přístroje n.e. Prague, CR), at pressure 6.5 MPa, flow 0.5 ml/min, rate of recorder 0.3 cm/min in mixture of solvents methanol:water, 8:2.

3. Results and discussion

3.1. Spectral characteristic of dyes in polymer matrices

The polystyrene (PS) and IPN absorb light up to 295 nm. Therefore, the monomer **IV** as donor exhibits absorption at the longest wavelength band at about 300 nm in these matrices only. In other polymer matrices the longest wavelength maximums in absorption spectra are nearly the same (Table 1). The monomer **VIII** as donor exhibits characteristic well-resolved absorption spectra for anthracene at 355, 370 and 389 nm. The maxima of absorption of bands are shifted bathochromically about 10 nm as compared with unsubstituted anthracene in all polymer matrices (Table 1).

Fluorescence spectrum of phenanthrene dye **IV** in polymer matrices shows emission in the region 335–370 nm (Table 1). In PE and IPN matrices, the positions of maximum are nearly the same. Positions of emission maximums of anthracene moiety (monomer **VIII**) are nearly the same as in unsubstituted anthracene only in IPN matrix. In the other polymer matrices, the emission bands are red-shifted by about 12 nm as compared with emission of unsubstituted anthracene.

Table 1
Absorption and emission characteristic of doped or terpolymerized monomers PhMMA and AMMA in polymer matrices

Probe	Medium[a]	λ_{abs}[b] (nm)	log ε[c]	λ_{em}[d] (nm)	Φ_r[e]	τ (ns)[f]	$G^{1/2}$[g]
PhMMA	PE	298	2.9	335, 352, 368	0.2	5.0	2.4
	PS	300	3.9				
	PMMA	298	3.8				
	PVC	300	3.8				
	IPN	300	3.9	335, 351, 367	0.02	3.5	8.8
AMMA	PE	388	2.7	392, 415, 439, 463	0.09	3.7	6.4
	PS	392	3.4	398, 421, 441	0.26	5.8	3.3
	PMMA	387	3.6	394, 416, 439	0.59	5.4	3.1
	PVC	393	3.4	396, 419, 442	0.52	5.4	3.7
	IPN	389	3.9	396, 418, 441	0.15	6.0	4.1

[a] PE: polyethylene, PS: polystyrene, PMMA: polymethyl methacrylate, PVC: polyvinyl chloride, IPN: interpenetrating polymer-like network (PE:P(S:BMA), 1:1(3:7)). Concentration = 0.002 mol kg^{-1} in polymer film, 10^{-4} mol kg^{-1} in IPN matrix.
[b] Maximum of longest wavelength absorption band.
[c] Molar extinction decadic coefficient of the longest wavelength absorption band.
[d] Wavelength at the maximum of emission band.
[e] Relative quantum yield to anthracene.
[f] Lifetime determined with deconvolution.
[g] Standard deviation (%).

3.2. Labeling of IPN

Derivatives of phenanthrene and anthracene, PhMMA and AMMA respectively, were used for labeling of IPN, which have polymerizable methacrylate double bond in their structure (Scheme 1). Therefore, these probes were linked to IPN by terpolymerization at the evolution of S-co-BMA network during the preparation of IPN. Applied monomeric fluorescence probes have similar structure and polarity as S and BMA monomer, which might lead to their random distribution in copolymer part. However, the way of preparation of the network by polymerization at elevated temperature of homogeneous solution of PE in the mixture of monomers S and BMA, cross-linker, initiator and fluorescent probes (IV and VIII) cannot secure the random distribution of fluorescence probes (see Section 2). Labeling of PE was performed by reaction of attached MAN with anthracene methanol before preparation of IPN. This reaction was carried out in xylene solution with catalytic amount of *p*-toluene sulfonic acid. Although short side chain of MAN might be formed at this technique of grafting of MAN at PE, we do not suppose linking of more than one anthracene structure unit at these sites because of the size of anthracene chromophore and steric effect of polymer chain. This reaction should result in random distribution of anthracene moiety in PE.

3.3. Energy transfer measurement

Absorption spectrum of IPN film with doped phenanthrene and anthracene is given in Fig. 1. Band (0, 0) at 302 nm belongs to transition $S_2 \leftarrow S_0$. Vibrationally resolved bands in the region 349–401 nm belong to transition $S_1 \leftarrow S_0$ of anthracene doped in this matrix. According these spectral data it is seen that there is a possibility to excite selectively phenanthrene around 300 nm and to follow the radiationless energy transfer in mixtures of polymers from phenanthrene to anthracene when the chromophores are freely added or bound to polymer chain. The mixture of

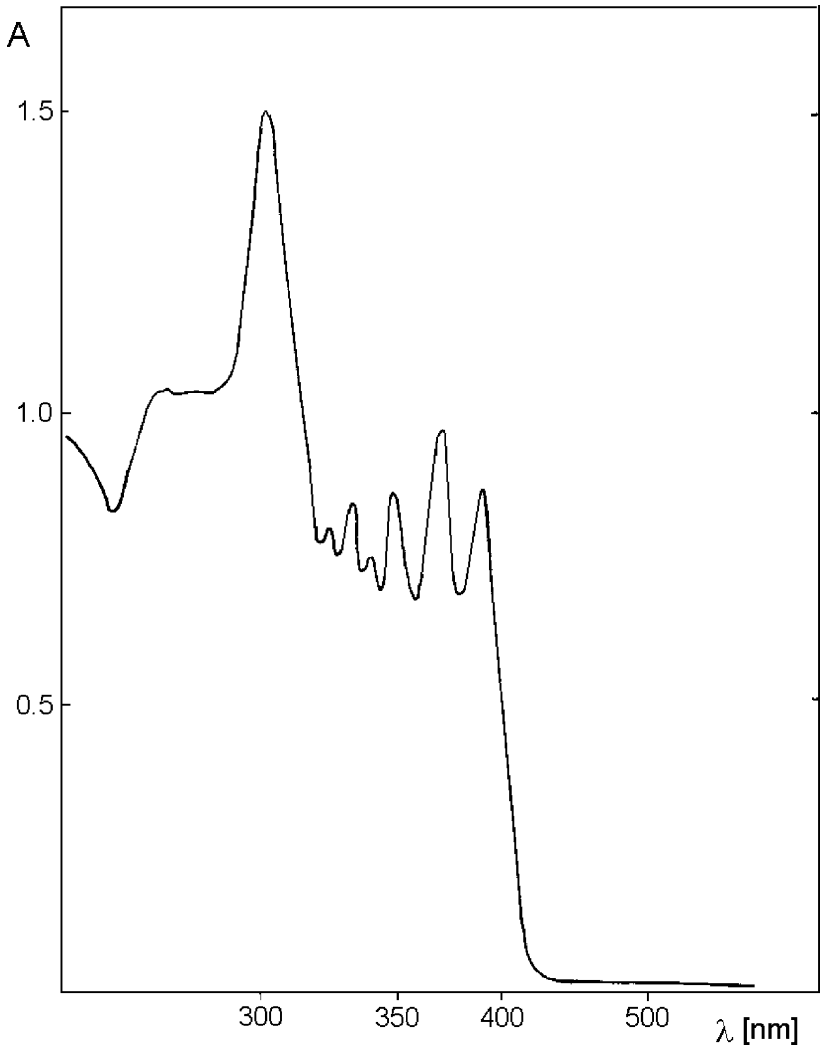


Fig. 1. Absorption spectrum of IPN film (PE:P(S:BMA), 1:1(3:7)), (1 mol% BDDM), (thickness 1 mm) doped with unsubstituted phenanthrene and unsubstituted anthracene. Concentration of probes: 1×10^{-2} mol kg^{-1}.

PhMMA and AMMA in the same concentration as the freely added chromophores in IPN blocs (Fig. 1) exhibits strong absorption. Probably the freely added phenanthrene and anthracene are partially lost during preparation as a result of high temperature (about 110 °C) during preparation or as a result of radical reaction. The main features of absorption spectra of mixture, however, are the same as in Fig. 1 but the absorption band of phenanthrene is slightly red-shifted (2 nm).

Fluorescence spectra of the mixture PhMMA and AMMA in IPN matrix exhibit emission in the region typical for anthracene chromophore. Emission spectrum of PhMMA in the region 340–400 nm was completely lost (Fig. 2). Clearly, there is an efficient transfer from excited chromophore phenanthrene to anthracene. This process was analyzed according to Perrin model of static quenching according to Eq. (3). Since Perrin model seems to be valid, it means that anthracene as acceptor lies in the sphere of active quenching R_s. Increasing concentration of anthracene in IPN leads to decreasing phenanthrene emission expressed as integral intensity F (Eq. (4)). The dependence of $\ln(F_0/F)$ on anthracene concentration is seen in Fig. 3. This set of data clearly shows that the dependence of $\ln(F_0/F)$ on acceptor concentration is curved. The initial slope (at low concentration of acceptor) is high (343 mol^{-1} kg) and calculated R_s is about 4.3 nm. When the curve is approximated by line passing through the origin, then the slope is lower (119 mol^{-1} kg), but the correlation coefficient is rather poor ($r = 0.92$). The calculated radius of active quenching R_s is about 3.1 nm. If the curve is approximated by a line at higher concentration of acceptor, then the slope is the lowest one (54 mol^{-1} kg) and the calculated $R_s = 2.3$ nm. This value is quite near the value of active sphere $R = 2.2$ nm determined previously for copolymer ethylene–methyl acrylate with attached pair phenanthrene–anthracene [6]. The differences in the value R_s are rather high indicating that our system as a result of preparation seems to be more complex. During preparation of IPN matrix, the copolymerization of four-component system (styrene, butyl methacrylate, 9-phenanthrene methyl methacrylate, 9-anthracene methyl methacrylate) occur. At this process the two probes are copolymerized predominantly into methacrylate blocs. Although the overall concentration is low the energy transfer is efficient as a result of the proximity of donor and acceptor. As the concentration of acceptor increases, the system becomes apparently more homogeneous. Moreover, high absorption does not allow determining the precise concentration of probes in IPN blocs after preparation. The concentration of probes is based on the weight entering the preparation of IPN blocs.

Consequently the determination of R_s in complex IPN system is loaded with large error (±50%), it indicates the limits of meaningful non-radiative energy transfer.

Measurement of NRET of bonded derivative PhMMA and AMMA in copolymer S-co-BMA of IPN confirmed pictures based on electron microscopy of these mixtures of polymers. They show that copolymer is fully homogeneous and no separation of phases occurs. Any phase separation larger than 3 nm forms barriers of efficient quenching and no efficient transfer would be observed.

This situation, where no NRET occurs, is observed when PhMMA is localized in the copolymer part by terpolymerization with S and BMA of IPN and anthracene is linked to PE. Two concentrations of anthracene, lower (7×10^{-4} mol kg^{-1}) and higher one (9×10^{-3} mol kg^{-1}), determined by absorption spectroscopy with equal phenanthrene concentrations were tested. Even at higher concentration of anthracene, no NRET was observed (Fig. 4),

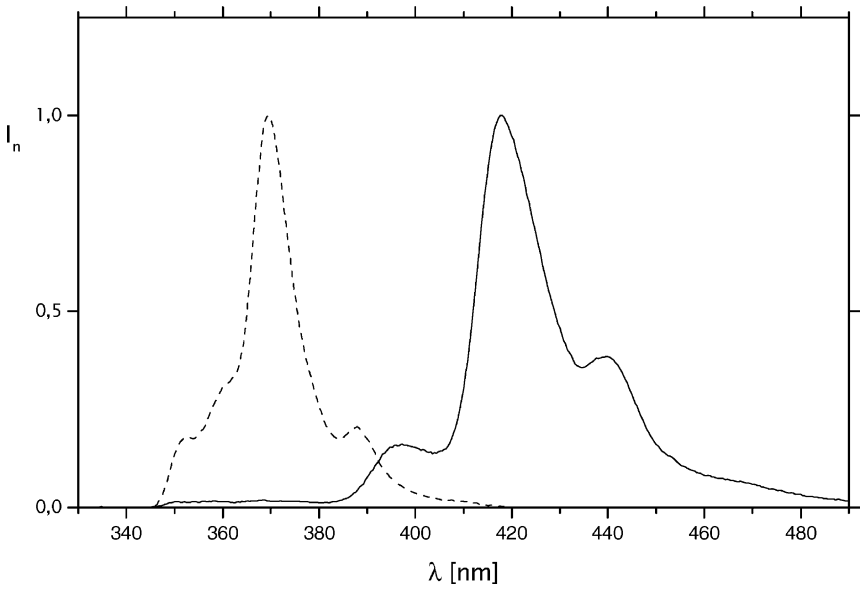


Fig. 2. Emission spectrum of PhMMA terpolymerized in IPN film (- - -), (thickness 1 mm) and mixture of PhMMA and AMMA terpolymerized in IPN film (—), (thickness 1 mm) excited at $\lambda_{ex} = 300$ nm. Concentration of PhMMA in films: 1×10^{-2} mol kg^{-1}, concentration of AMMA: 2×10^{-2} mol kg^{-1}.

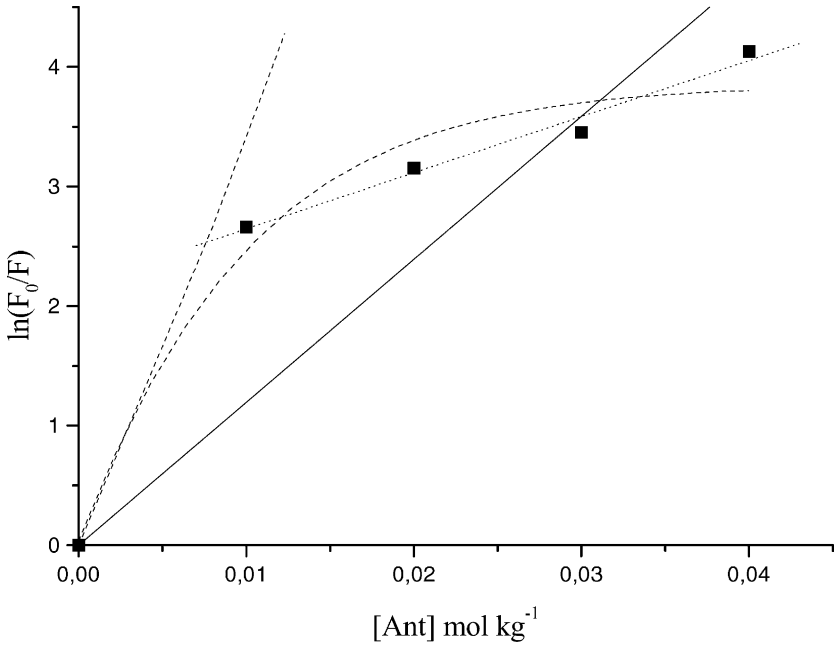


Fig. 3. Plot of $\ln(F_0/F)$ vs. bulk concentration of anthracene [Ant] at non-radiative energy transfer. The slope of linear curve fitted through origin (—) calculated by linear regression with correlation coefficient $r = 0.92$ is 119 mol^{-1} kg. The slope at the beginning of dashed curve (- - -) is 343 mol^{-1} kg. The slope of dotted linear curve (···) calculated by linear regression with $r = 0.98$ is 54 mol^{-1} kg.

although this concentration should be sufficient for efficient energy transfer. The emission spectrum in Fig. 4 at 300 nm excitation shows phenanthrene fluorescence solely and the intensity of phenanthrene fluorescence without acceptor at the same concentration was nearly equal (Fig. 2). PE with linked anthracene forms continual phase in IPN in which cell-like domains with bound phenanthrene of the size 100 nm are separated [11]. This microscopic arrangement forms a barrier for energy transfer between chromophores localized in the different phases. If there is any interphase in IPN, some energy transfer would be observed by time-resolved emission spectroscopy. In this case, small changes in lifetime of phenanthrene report any extent of energy transfer.

Measurements on model systems of free added phenanthrene and anthracene confirmed the previous results and

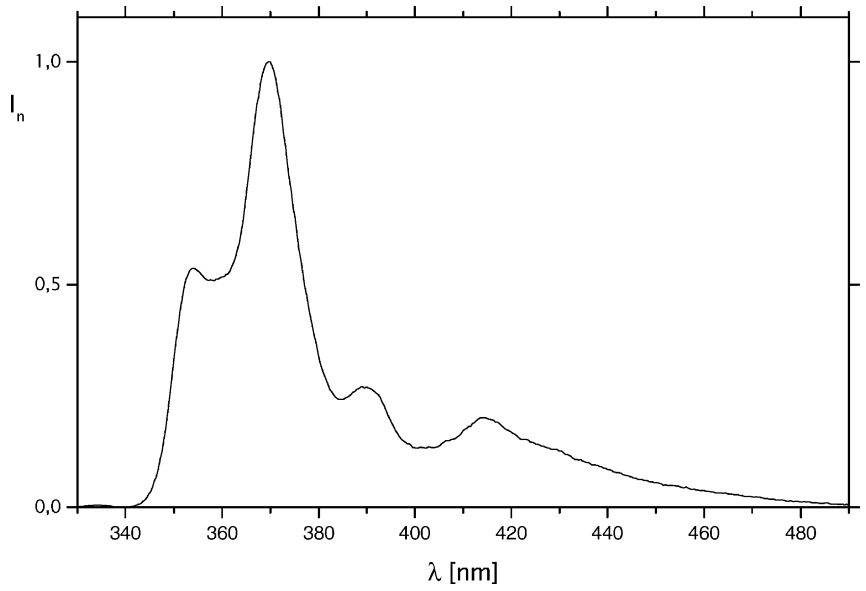


Fig. 4. Emission spectrum of mixture of PhMMA attached in copolymer phase of IPN and anthracene attached to PE at excitation wavelength $\lambda_{ex} = 300$ nm. Concentration of PhMMA: 1×10^{-2} mol kg^{-1}, concentration of anthracene: 9×10^{-3} mol kg^{-1}, thickness of film: 1 mm.

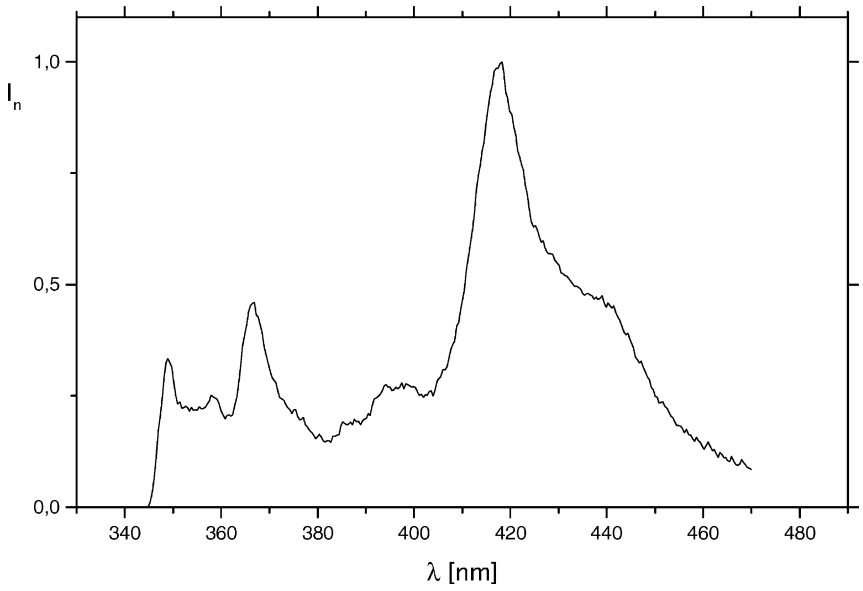


Fig. 5. Emission spectrum of IPN doped with mixture of phenanthrene and anthracene at excitation wavelength $\lambda_{ex} = 300$ nm. Concentration of chromophores were 1×10^{-2} mol kg^{-1}, thickness of film: 1 mm.

analysis of microscopic pictures [11]. In Fig. 5 there is emission spectrum of mixture of phenanthrene and anthracene in IPN of equal chromophore concentration. Clearly, the energy transfer occurs according to this spectrum but it is not complete as the presence of bands in the region 345–370 nm belonging to phenanthrene indicates. At the preparation of the network part of chromophores is located in the amorphous phase where it is closed. At doping of semi-crystalline polymers with low molecular compounds, these additives are concentrated outside the crystalline phase. Similarly, the barrier for energy transfer in IPN is caused by separation between PE and copolymer S-co-BMA. Pictures of atomic force microscopy [11] show crystalline lamellas of PE of 25 nm length which are located between domains of copolymers in IPN and consequently they prevent intruding of chromophores in the interface region of IPN.

4. Conclusion

Using Perrin equation, which is based on simple model of static fluorescence quenching between donor and acceptor, radius of active sphere of quenching was determined for pair of bound probes PhMMA and AMMA in IPN. Dependence donor fluorescence expressed as $\ln(F_0/F)$ on the acceptor concentration confirm the energy transfer in copolymer S-co-BMA and the slope yields radius of active sphere of quenching. In this system there is more efficient quenching than proportional at low concentration of anthracene (under 0.01 mol kg^{-1}). This might be caused by the fact that the distribution of chromophores is not fully random.

Energy transfer between phenanthrene chromophore (PhMMA) bound in copolymer S-co-BMA and anthracene chromophore linked on PE does not occur. This confirms the two-phase structure IPN in nano-range. These results of energy transfer do not yield any indication for third interpenentrated phase in this system, although this phase was confirmed by electron microscopy [11]. It is due probably by very small volume of this phase.

Acknowledgements

Authors thank grant agency VEGA of Slovak Republic for financial support through grants 2/7009/20 and 2/5035/99.

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