

Synthesis and Spectral Characteristics of the Free and Bound Luminophore Derived from Bromophenanthrene

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Friedel—Crafts acylation of 9-bromophenanthrene with 3-chloropropanoyl chloride yielded 3-(3-chloropropanoyl)-9-bromophenanthrene that was used to prepare 3-propenoyl-9-bromophenanthrene. Radical copolymerization of the latter compound with styrene, methyl methacrylate, and ethyl acrylate yielded statistic copolymers.

The spectral properties of the new 3-acyl-9-bromophenanthrene type of luminophore were compared with the ones of derivatives of phenanthrene and anthracene in polymer matrix at 77 K and laboratory temperature. As opposed to the parent hydrocarbons the new luminophore exhibits the phosphorescence exclusively ($\lambda_{\max} \approx 520$ nm) both at laboratory temperature and 77 K. The lifetime of emission at 77 K is about 8 ms and the decay is monoexponential.

Recently the phenanthrene as free and bound chromophore was used for a study of transfer of energy and formation of exciplexes [1—3]. Also the kinetics of the decay was followed in the presence of oxygen in a matrix of poly(methyl methacrylate) (PMMA) [4].

Looking for new types of chromophores performing high absorption in UV area combined with high photochemical reactivity or emission, we have functionalized phenanthrene. A combination of substituents, such as bromine and alkylcarbonyl on phenanthrene provided a structural unit of interesting spectral properties. Bromine being a substituent with the effect of heavy atom, increases the yield of triplet state. The triplet state of 3-alkanoylphenanthrene is of the $\pi-\pi^*$ type and is not photochemically active. Therefore the combination of the two substituents on phenanthrene facilitates a high phosphorescence.

The goal of this work is the preparation of the new type of chromophore and its basic spectral characterization in the solid phase.

EXPERIMENTAL

9-Bromophenanthrene (I) was prepared by bromination of phenanthrene according to [5]. Recrystallization from hexane yielded the product with m.p. = 55—59 °C (Ref. [6] gives m.p. = 57—60 °C).

3-(3-Chloropropanoyl)-9-bromophenanthrene (II) was prepared as follows: To a stirred solution of 9-bromophenanthrene (60 g; 0.23 mol) and 3-chloropropanoyl chloride (42.9 g; 0.23 mol) in 380 cm³ of CS₂ AlCl₃ (77.2 g; 0.58 mol) is slowly added at the

temperature 4—7 °C. At the same temperature the reaction mixture is stirred for another 20 min. The dark solid product is decomposed by slow addition of ice and hydrochloric acid. After extraction with 700 cm³ of CHCl₃ and solvents evaporation at reduced pressure the product of m.p. = 118—150 °C was obtained. Recrystallization from acetone after boiling with active carbon yielded 49 g (60 %) of the product with m.p. = 133—138 °C. The purity of the product was examined by thin-layer chromatography (eluent: benzene—heptane, $\varphi_r = 1 : 1$) and by liquid chromatography. For C₁₇H₁₂OClBr ($M_r = 374.64$) w_i (calc.): 58.73 % C, 3.23 % H; w_i (found): 58.97 % C, 3.02 % H. IR spectrum (CHCl₃), $\tilde{\nu}/\text{cm}^{-1}$: 1680 (CO), 1615, 1530 (C=C), 1420, 1190 (CHCH₂). UV spectrum (CHCl₃), λ_{\max}/nm ($\log \{\epsilon\}$): 322.6 (4.41). ¹H NMR spectrum (CDCl₃), δ : 3.61 (t, 2H, CH₂Cl), 4.03 (t, 2H, CH₂CO), 7.69—7.78 (m, 2H, H-6, H-7), 7.81 (d, 1H, H-5), 8.09 (s, 1H, H-10), 8.11 (d, 1H, H-8), 8.37 (d, 1H, H-1), 8.72 (d, 1H, H-2), 9.21 (s, 1H, H-4). Mass spectrum, m/e : 350, 348, 346 (M^+), 312, 310, 286, 284, 178, 176, 106.

3-Propenoyl-9-bromophenanthrene (III) was prepared as follows: 3-(3-Chloropropanoyl)-9-bromophenanthrene (3 g; 0.0086 mol) is dissolved in a mixture of 100 cm³ of acetonitrile and 50 cm³ of CHCl₃. During stirring at laboratory temperature anhydrous potassium acetate (3.98 g; 0.0345 mol) is added and the reaction mixture is stirred for 4 h. Since according to liquid chromatography the mixture still contains the parent compound, it is heated to 50 °C and stirred at this temperature for 1.5 h. The parent compound is completely decomposed. After the acetic acid neutralization by sodium carbonate (0.91 g; 0.0086 mol) in 15 cm³ of water, the

organic part is separated and concentrated under vacuum. Thus 2.9 g of the raw product of m.p. = 102–111 °C is obtained. Chromatographic separation on silica gel column (Kavalier, Sázava, CR L 40/100) with petroleum ether—benzene ($\varphi_r = 1 : 1$) as eluent yielded 2.6 g (97 %) of 3-propenoyl-9-bromophenanthrene of m.p. = 102–111 °C. Crystallization from acetonitrile, resp. acetone did not change the melting point of the product. The reason for the wide melting region is probably the formation of solid polymer. The purity of product was followed by thin-layer chromatography (benzene—heptane, $\varphi_r = 1 : 1$) and liquid chromatography. For $C_{17}H_{10}Br$ ($M_r = 311.18$) $w_i(\text{calc.})$: 65.61 % C, 3.56 % H, 25.68 % Br; $w_i(\text{found})$: 65.48 % C, 3.91 % H, 23.55 % Br. UV spectrum ($CHCl_3$, λ_{max}/nm ($\log \{\epsilon\}$): 259.8 (3.8), 331.1 (3.41). IR spectrum ($CHCl_3$, $\tilde{\nu}/cm^{-1}$: 1680 (CO), 1630, 1530 (C=C), 990 (=C—H, $CH_2=CH-$). 1H NMR spectrum ($CDCl_3$, δ : 6.03, 6.04, 6.06, 6.07 (dd, 1H, H—C=C, *trans* to carbonyl); 6.54, 6.55, 6.58, 6.59 (dd, 1H, H—C=C, *cis* to carbonyl); 7.33, 7.35, 7.37, 7.41 (dd, 1H, =CH—CO), 7.69—7.81 (m, 2H, H-6, H-7); 7.85 (d, 1H, H-5), 8.11 (s, 1H, H-10), 8.13 (d, 1H, H-8); 8.39 (d, 1H, H-1), 8.75 (d, 1H, H-2), 9.23 (s, 1H, H-4). Mass spectrum, m/z : 312, 310, (M^+) 285, 283, 177, 149.

The copolymers of 3-propenoyl-9-bromophenanthrene with methyl methacrylate (MMA), ethyl acrylate (EA), and styrene (S) were prepared as follows: The mixture of 3-propenoyl-9-bromophenanthrene (0.5563 g), methyl methacrylate (15.76 g) resp. ethyl acrylate (13.9 g) resp. styrene (14.1 g) and 2,2-azobis(isobutyronitrile) (0.01 g) was polymerized in sealed ampoule under inert atmosphere in the dark at laboratory temperature for 8 d. After threefold precipitation in the system benzene—methanol and drying to constant mass the yield was 0.9 g (5.51 %). The polymerization took place in the dark for 12 d for ethyl acrylate and 6 d for styrene. We have received 1.3 g of copolymer in the case of ethyl acrylate (8.99 %) and 1.3 g in the case of styrene (8.89 %).

The absorption spectra in the UV region were measured by M-40 equipment (Zeiss, Jena). IR spectra were measured by IR-75 and M-80 apparatus (Zeiss, Jena). The elemental analysis was carried out in automatic equipment (Heraus, Hanau, FRG). 1H NMR spectra were measured in the apparatus AM-300 (Bruker, FRG) in deuteriochloroform with tetramethylsilane as internal standard at 30 °C. The mass spectra were recorded by JMFD 100 apparatus (Jeol, Japan). The purity of products was checked by a thin-layer chromatography on Silufol 254 (Kavalier, Sázava, Czech Republic) and liquid chromatography on Merckogel PVA 500 (column 500 mm \times 9 mm) and Separon SE (column 250 mm \times 4 mm), with methanol as eluent and UV detection

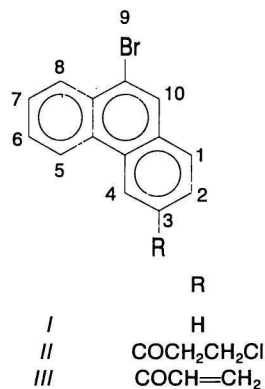
at 254 nm. The copolymers were analyzed by GPC in columns filled by porous glass in THF and calibrated by polystyrene standard. The melting points were determined by an apparatus of Boetius type and are not corrected.

The emission spectra of low-molecular compounds doped into both polymers and polymers in the form of films were measured by apparatus composed of accessible optical and electrical parts [7] and connected to microcomputer [8], at laboratory temperature and at 77 K. Front-face photomultiplier EMI 5256S was used as a detector. The lifetime of excited states in micro- and millisecond region was determined in single-pulse regime in the equipment described previously [9]. The decay curves were evaluated as monoexponential. The quality of fitting was checked by the value of correlation coefficient which was always better than 0.99; and by standard deviation of experimental and calculated curve that was always better than 5 %. Absorption spectra of transients were measured by the equipment described in the paper [10]. Ruby laser (Konrad model K1QS2) together with doubler of frequency provided flashes with half-width of 20 ns and wavelength 347 nm. Irradiation was carried out in silica cells. Before irradiation, the solutions were bubbled with argon. The equipment was calibrated to extinction coefficient of triplet of naphthalene.

RESULTS AND DISCUSSION

Synthesis of Monomer and Copolymers

The structure of the prepared low-molecular compounds is shown in Formula 1. 9-Bromophenanthrene (*I*) was prepared by bromination of phenanthrene [5]. By Friedel—Crafts acylation of *I* with 3-chloropropanoyl chloride 3-(3-chloropropanoyl)-9-bromophenanthrene (*II*) was prepared in 60 % yield. The monomer 3-propenoyl-9-bromophenanthrene (*III*) was obtained by dehydrochlorination of *II* with



Formula 1

Table 1. Characteristics of the Copolymers of 3-Prnnoyl-9-bromophenanthrene (*III*) with Methyl Methacrylate (MMA), Ethyl Acrylate (EA) and Styrene (S).

Copolymer	Content of PBrP	M_r^a
	mass %	
Poly(<i>III</i> -co-MMA)	56	4 000 000
Poly(<i>III</i> -co-EA)	39	910 000
Poly(<i>III</i> -co-S)	32	725 000

a) M_r corresponds to the position of maximum of GPC trace in THF. The system was calibrated by polystyrene standards.

potassium acetate. Acylation of 9-bromophenanthrene by acetyl chloride under the same conditions [6] as used in this work leads to acylation to the position 3. The assumption that 3-(3-chloropropanoyl)-9-bromophenanthrene is formed by acylation with 3-chloropropanoyl chloride is confirmed by the ^1H NMR spectra. In the spectrum it is possible to ascribe unequivocally the singlet at $\delta = 9.21$ to aromatic proton in the position 4, singlet at $\delta = 8.09$ to proton in the position 10 and multiplet at $\delta = 7.69$ — 7.78 to two protons in the positions 6 and 7. The remaining four doublets were ascribed to H-5, H-8, H-1, and H-2 in respect to the deshielding effect of carbonyl group. Radical copolymerization of the monomer *III* with styrene, methyl methacrylate, and ethyl acrylate provides corresponding copolymers containing 30—50 mass % of compound *III* with high molecular mass (Table 1). In principle, we can say that copolymerization of the monomer *III* proceeds in a similar way as with other arylvinyl ketones [11].

Spectral Measurements

Absorption and emission spectra of derivatives of aromatic hydrocarbons have been well characterized mainly in solution [12]. Less attention was paid to the spectra in the solid matrices [13]. For characterization of 3-acyl-9-bromophenanthrene chromophore, both free and bound into a macromolecule, emission spectra of derivatives of anthracene and phenanthrene were compared. Spectral measurements in the solid matrices can be complicated by the aggregation. The molality of 0.1 mol kg^{-1} is a compromise between the intensity of a signal of dopant and its solubility. To evaluate the influence of substituents on photophysical processes of these chromophores, we introduce relative quantum yield of emission ϕ_r . This variable was determined as a ratio of integral of emission spectrum or a part of it, and the integral of emission spectrum of anthracene under the given conditions. Anthracene was chosen because its emission spectrum is very little dependent on conditions. Since the emission spectra are measured in frontal arrangement and under excitation at 313 nm, at which all derivatives show high absorption ($A >$

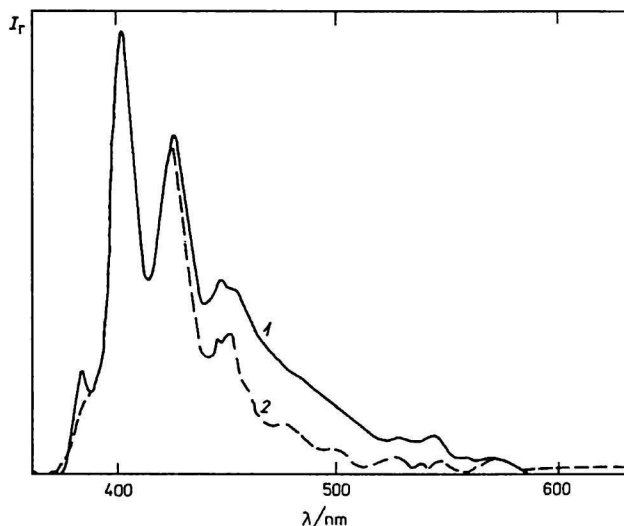


Fig. 1. Emission spectrum of anthracene doped into PMMA film at 77 K (1) and laboratory temperature (2).

2), the relative quantum yields reflect the influence of substituents on photophysical processes.

With anthracene no difference in emission spectra is observed at 77 K and laboratory temperature (Fig. 1). In emission spectra, fluorescence prevails unambiguously, with the yield that is not significantly influenced by temperature. A very weak phosphorescence of anthracene in solution was observed by *Grellmann* and coworkers at 670 nm [14]. Substitution of bromide to the position 9 of anthracene leads to a decrease of fluorescence [12] at laboratory temperature. At 77 K the intensity of fluorescence of 9-bromoanthracene is comparable to unsubstituted anthracene (Table 2). Under our experimental conditions we did not observe emission above 600 nm that is characteristic of phosphorescence. It means that the radiation decay of triplet of anthracene and 9-bromoanthracene occurs very inefficiently in the interval 77—300 K.

At laboratory temperature, phenanthrene as well as anthracene exhibit fluorescence only. The intensity of phenanthrene fluorescence is lower in comparison with anthracene. At 77 K in the case of phenanthrene, on the other hand, an intense phosphorescence is observed together with the fluorescence (Fig. 2). The overall yield of emission is comparable to anthracene (Table 2). At laboratory temperature the substitution by bromide in phenanthrene leads to significantly lower fluorescence in comparison with unsubstituted phenanthrene and only very weak phosphorescence is observed. It noticeably increases at 77 K. We can say that the radiation decay of triplet state phenanthrene is more efficient than that of anthracene and it is increased even more by the effect of heavy atom, mainly at 77 K.

In the region of about 520 nm, in which phosphorescence of phenanthrene and 9-bromophen-

Table 2. Spectral Characteristics of Chromophores of the Anthracene and Phenanthrene Type in Polymer Matrix

Temperature	Chromophore $\lambda_{\text{max}}/\text{nm}$	ϕ_f	τ/ms
Anthracene			
laboratory	387, 402, 425, 450	1.00	
77 K	386, 403, 428, 450	1.00	
9-Bromoanthracene			
laboratory	416	0.06	
77 K	397, 419, 445	0.80	
Phenanthrene			
laboratory	366, 385, 399, 424, 449	0.16	
77 K	364, 378, 383, 399, 422	0.39 ^a	3 500
	460, 496, 533, 544	0.22 ^b	
9-Bromophenanthrene			
laboratory	400, 520	0.02	
77 K	483, 491, 520	0.23	10.2
3-(3-Chloropropanoyl)-9-bromophenanthrene			
laboratory	519	0.02	
77 K	511, 544	0.59	8.2
3-Propenoyl-9-bromophenanthrene			
laboratory	411, 520	0.03	
77 K	519, 544	0.73	9.4
Poly(3-propenoyl-9-bromophenanthrene-co-MMA) ^c			
laboratory	523	0.05	
77 K	516, 545	0.59	8.4
Poly(3-propenoyl-9-bromophenanthrene-co-S) ^c			
laboratory	401, 517	0.04	
77 K	520	0.87	7.9
Poly(3-propenoyl-9-bromophenanthrene-co-EA) ^c			
laboratory	405, 520	0.03	
77 K	523, 546	1.67	7.7

a) Total emission; b) phosphorescence; c) Copolymers (10 mg) were doped into PMMA film (50 mg).

anthrene is observed, one can follow also emission of 3-alkanoyl-9-bromophenanthrene derivatives (Fig. 3). The phosphorescence shows two maximums with the fluctuating ratio. They are most pronounced at 77 K. Rather high relative emission is observed for 3-(3-chloropropanoyl)-9-bromophenanthrene in polymer matrix at laboratory temperature; it is 25 times increased at 77 K. 3-Propenoyl derivative shows weaker emission under laboratory temperature. Binding of complex chromophore of the phenanthrene type into a macromolecule does not lead to the principal change of emission spectra (Fig. 4). In comparison with 9-bromophenanthrene, free and bound 3-alkanoyl derivatives exhibit higher phosphorescence at laboratory temperature and 77 K. The fact that the emission of both the model compound and bound structural unit is the same suggests that this chromophore is not influenced by the environment.

The lifetime of the fluorescence of anthracene and phenanthrene in PMMA matrix at laboratory temperature is 2.7 ns and 3.3 ns, respectively. The lifetime

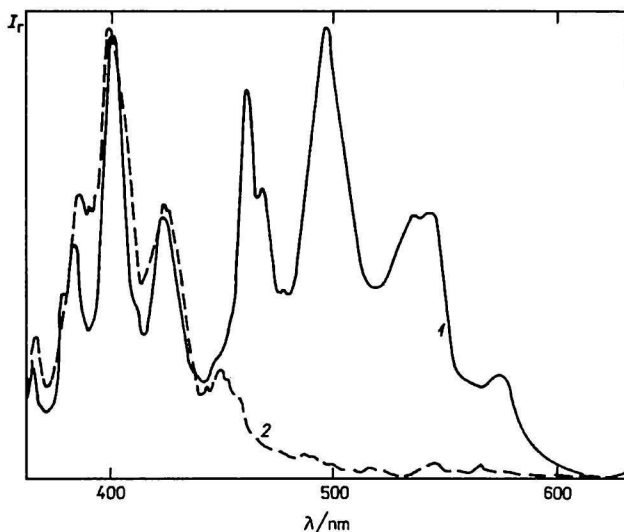


Fig. 2. Emission spectrum of phenanthrene doped into PMMA film at 77 K (1) and laboratory temperature (2).

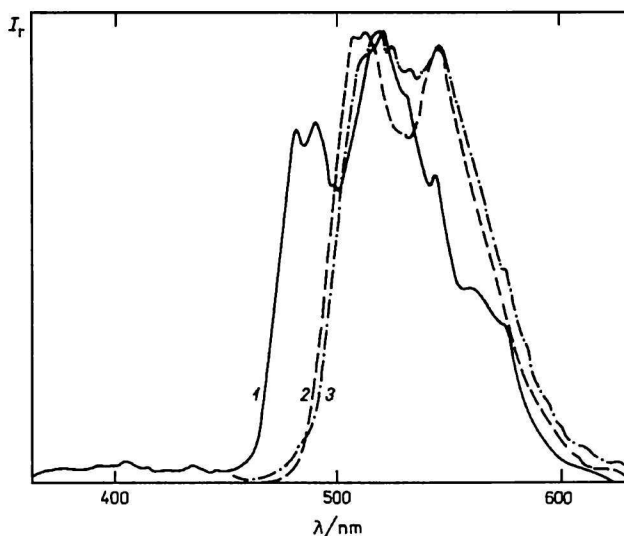


Fig. 3. Emission of derivatives of 9-bromophenanthrene substituted in the position 3 and doped into PMMA film at the temperature 77 K when 1. X = H, 2. X = COCH₂CH₂Cl, and 3. X = COCH=CH₂.

of phosphorescence 3.5 s of nonsubstituted phenanthrene in PMMA matrix at 77 K [4] is almost by three orders of magnitude longer than that of 9-bromophenanthrene (Table 2). The shortening of the lifetime is caused by the effect of heavy atom. Substitution by alkylcarbonyl does not significantly influence this lifetime. The decay of emission of chromophores of 3-alkanoyl-9-bromophenanthrene, both free and bound, is monoexponential in polymer matrix at 77 K. The decay does not reflect the incompatibility that is obvious from cloudiness of films as we dope the copolymer into the matrix of PMMA.

The absorption spectra of transients were measured in a solution of dichloromethane in inert at-

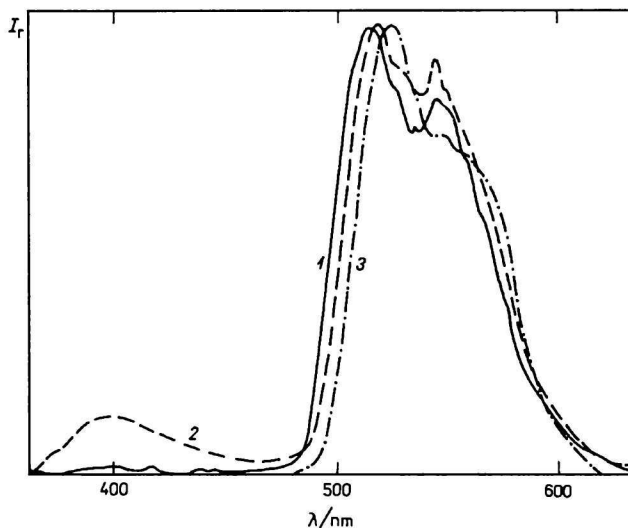


Fig. 4. Emission of the copolymers of 3-propenoyl-9-bromophenanthrene with 1. MMA, 2. S, and 3. EA (10 mg) doped into the PMMA films (50 mg) at 77 K.

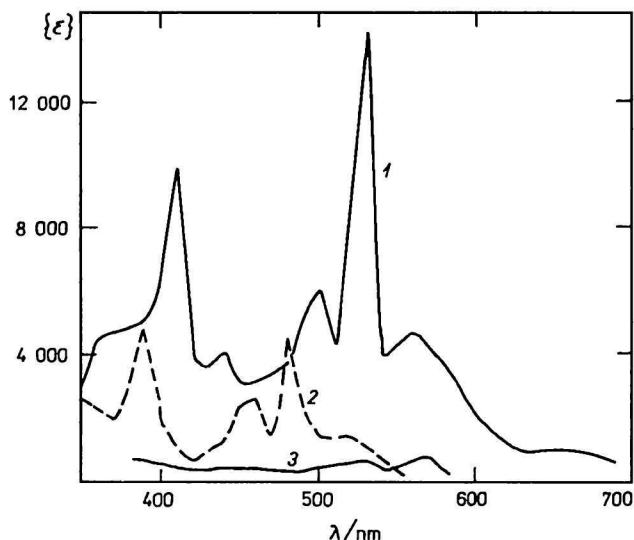


Fig. 5. Absorption spectra of transients immediately after the flash in dichloromethane solution in argon at laboratory temperature. 1. 3-(3-Chloropropanoyl)-9-bromophenanthrene; 2. 9-bromophenanthrene; 3. poly(3-propenoyl-9-bromophenanthrene-co-MMA).

mosphere under laboratory temperature. The most intense absorption spectrum of the triplet state is followed for 3-(3-chloropropanoyl)-9-bromophenanthrene (Fig. 5). Very weak absorption spectrum is observed for bound chromophore in the copolymer. This observation suggests that in the solution at laboratory temperature the binding of chromophores leads to extensive self-quenching, that is deactivation of excited structural units with the same unit in the ground state. Considerable extent of self-quenching of tri-

plet states of chromophores bound into macromolecules was observed for poly[(4-diphenyl)- and (2-naphthyl)-2-propen-1-on] [15].

At the laboratory temperature the low intensity of emission of 3-alkanoyl-9-bromophenanthrene chromophore in films is probably not caused by the self-quenching, because the polymers exhibit higher phosphorescence than the low-molecular substances. The reason of the lower intensity is mainly efficient temperature-dependent radiationless process typical for this chromophore as well as quenching caused by the presence of such quenchers as oxygen and other impurities.

Finally we can conclude that a rather simple procedure yields a chromophore of similar spectral qualities as benzil [16]. Moreover, in the process of polymerization it is easier to build it to the chain of macromolecule. The possibilities of utilization of 3-alkanoyl-9-bromophenanthrene for spectral studies as triplet probe in the study of polymer preparation and properties are being examined.

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