= PHOTOCHEMISTRY =

Photoreduction of 9,10-Phenanthrenequinone in the Presence of Dimethacrylate Oligomers and Their Polymers

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Abstract—The effective rate constants for the photoreduction (k_H) of 9,10-phenanthrenequinone (PQ) in the presence of dimethacrylate monomers (ethylene glycol dimethacrylate (DMEG), triethylene glycol dimethacrylate (TGM-3), and oligocarbonate dimethacrylate (OKM-2)) and porous polymers based on them have been spectrophotometrically determined. The values of k_H in the presence of DMEG and TGM-3 in benzene solutions and in the monomer media are two times greater than in the presence of OKM-2. The values of k_H for PQ in pores of polyDMEG, polyTGM-3, and polyOKM-2 are approximately identical and do not depend on the pore size (up to hundreds of nanometers) and the specific surface area.

Porous polymer matrices find wide application in the production of adsorbents [1−3] and membranes [4], in microelectronics [5], and in medicine [6], as well as in the creation of catalysts [7] and polymer-supported reagents [8, 9], thereby predetermining the interest in comparative studies of the reactivity of chemical compounds in solution and in the pore surface layer. One of the tasks of modern materials science is the creation of materials with locally altered properties of a macrohomogeneous polymer (block), in particular, a porous polymer. Such a modification under mild conditions can be carried out via photochemical transformations induced by visible light, namely, photochemical reactions of carbonyl compounds (Q) in the presence of hydrogen donors (DH) to form the reactive products QH $\cdot$ and D $\cdot$ [10]. Earlier we demonstrated this possibility using photomodification of film materials as an example [11] and studied the photoreduction kinetics of the same *o*-quinone moiety in a monomer molecule, its linear homopolymer, and a grafted layer on the pore surface of the porous polymer (hydrogen donors N,N-dimethylanilines); in that case, the quinone units that had been already grafted to the polymer chain underwent modification, which consisted in their reduction to the corresponding pyrocatechols. Radicals D $\cdot$, which are generated during the photoreduction of carbonyl compounds, can be used for the subsequent modification of the hydrogen donor by radical chain processes; in particular, if polymer materials are used as a hydrogen donor, this can lead to a change in their properties

(photoinduced polymer grafting) [12, 13]. The key stage of this process is the photoreduction of carbonyl compounds by the polymer. Benzophenone and its derivatives are commonly used for this purpose, and the modification is carried out using UV radiation. In this study we investigated the kinetics of photoreduction with visible light of 9,10-phenanthrenequinone (PQ) in solutions, in dimethacrylate monomer media, and in the pores of thick porous polymers obtained from the monomers. The monomers used were ethylene glycol dimethacrylate (DMEG), triethylene glycol dimethacrylate (TGM-3), and oligocarbonate dimethacrylate (OKM-2). The structural formulas of PQ and the monomers are shown in Fig. 1.

EXPERIMENTAL

Ethylene glycol dimethacrylate DMEG (Aldrich), triethylene glycol dimethacrylate TGM-3 (Aldrich), and α,ω-bis(methacryloyloxyethylenoxycarbonyloxy)ethyleneoxyethylene OKM-2 (Reper-NN) were purified according to known procedures. Block samples of 2 mm in thickness of porous polymers based on DMEG, TGM-3, and OKM-2 were synthesized by photopolymerization of monomer−blowing agent compositions according to previously described procedures [14, 15]. The solvents benzene and 1,2-dichlorobenzene were purified according to conventional procedures [16].

The PQ photoreduction kinetics were studied spectrophotometrically by monitoring the decrease in
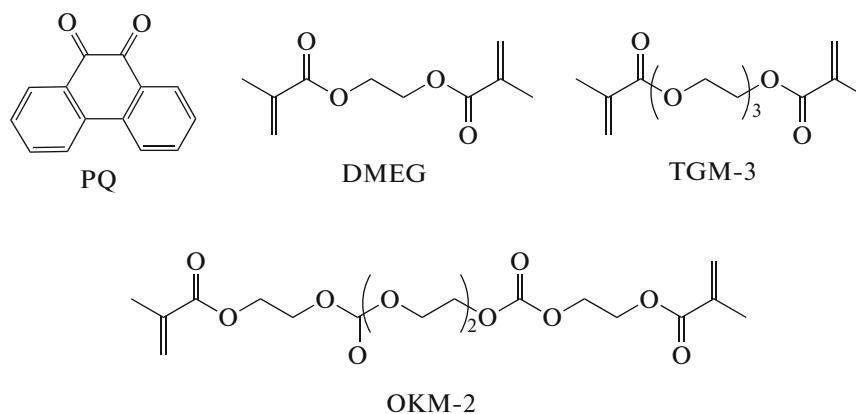
Fig. 1. Structural formulas of 9,10-phenanthrenequinone and the dimethacrylates used in the work.

intensity of the PQ absorption band at $\lambda_{max} = 412$ nm in accordance with the Bouguer–Lambert–Beer law. The electronic absorption spectra were recorded on a LOMO-Spektr SF-56 spectrophotometer. A KGM-24-150 lamp with a focusing device was used for photoirradiation. Phenanthrenequinone solutions in the monomers and monomer–benzene mixtures were photoirradiated in a spectrophotometric cell with $l = 1.0$ cm at a distance of 6 cm from the focusing device; the luminous intensity was 13 kcd. The porous polymer samples were made transparent by impregnating them in an immersion liquid, which was a benzene and 1,2-dichlorobenzene blend (60 vol % benzene and 40 vol % 1,2-dichlorobenzene for polyTGM-3 and polyDMEG or 90 vol % benzene and 10 vol % 1,2-dichlorobenzene for polyOKM-2). For kinetic experiments, a 2-mm thick porous polymer block was placed in a spectrophotometric cell with $l = 3$ mm, which was filled with a PQ solution in the immersion liquid and, when the sample became transparent, it was photoirradiated as described above.

The surface of the resulting polymer samples was analyzed using the AFM technique with Smena-A NT-MDT and Solver P47 microscopes by scanning in the tapping mode. The scale analyzed ranged from hundreds of nanometers to microns. The characteristic average size of inhomogeneities in the polymer structures was found from an autocorrelation function of the spatial distribution of the topographic features, revealed by AFM, as the width of the autocorrelation function.

The BET specific surface area of the porous polymers (S_{sp}) was determined chromatographically by thermal desorption of nitrogen [17] using a GKh-1 gas meter (Russia). The commercial adsorbent Silochrome S-80 with a specific surface area of 80 m^2/g was used as a reference. The experiment was repeated at least three times for each of three different values of relative nitrogen pressure in the nitrogen–helium mixture, and S_{sp} was calculated for each sample.

RESULTS AND DISCUSSION

The irradiation of benzene solutions of 9,10-phenanthrenequinone and the dimethacrylates with visible light leads to a change in the color of the solutions, which is associated with the PQ photoreduction reaction via hydrogen atom abstraction from the monomer molecule. This process underlies the initiation of photopolymerization of acrylic monomers [18, 19]. As a typical example, Fig. 2 shows the changes in the spectral characteristics of a PQ and DMEG solution in benzene by its irradiation with visible light. It is seen that the decrease in the intensity of the quinone absorption band at 410 nm is accompanied by an increase in the absorbance of the solution in the UV region of the spectrum, with distinct isosbestic points being observed at $\lambda = 360$ and 370 nm.

In the photoreduction of 9,10-phenanthrenequinone, the active state is the lowest excited triplet to which the quinone molecule converts from the $S(\pi\pi^*)$ and $S(n\pi^*)$ states [20]. In the electronic absorption spectrum of 9,10-phenanthrenequinone, the bands corresponding to the $S(\pi\rightarrow\pi^*)$ and $S(n\rightarrow\pi^*)$ electronic transitions have maxima at 410 ($\varepsilon = 2200$ L mol^{-1} cm^{-1}, benzene) and 510 nm, respectively. The PQ photoreduction products are the corresponding phenol ethers and ketols [21], which have a weak yellow color ($\varepsilon \sim 10$ L mol^{-1} cm^{-1} at $\lambda = 410$ nm [22]) so that the kinetics of its photoreduction can be studied spectrophotometrically by monitoring the decrease in PQ absorbance at $\lambda_{max} = 410$ nm.

The experiments have shown that the kinetics of the PQ photoreduction reaction in the presence of dimethacrylates in benzene solutions and in the monomer media is described by a first-order rate law in all the cases. The obtained values of the effective rate constants for the photoreduction of PQ (k_H) are given in Table 1. The rate constant of PQ photoreduction in benzene is 0.2×10^{-3} s^{-1}.

The data in Table 1 show that the value of k_H in the photoreduction of PQ in the benzene solution of each

dimethacrylate increases with increasing monomer concentration and tends to k_H in the monomer medium. In the presence of TGM-3, the value of k_H in the solution becomes the same as in the monomer medium (entry no. 10) already at a 500-fold molar excess of the monomer (no. 8). In the DMEG and OKM-2 solutions, this is not achieved even at the 1000-fold monomer excess (nos. 3 and 16). Comparison of the data for the monomers DMEG and TGM-3 characterized by the same type of oligomeric block shows the following. At a [PQ] : [monomer] ratio of 1 : 10, k_H in the presence of TGM-3 is approximately three times that in the presence of DMEG (with allowance for k_H in benzene) (nos. 1, 5). As the concentration of the monomers increases, the difference in k_H decreases and completely disappears when the reaction is carried out in the monomer medium (nos. 4, 10). It can be assumed that at low monomer concentrations, the k_H value is determined by the number of hydrogen atoms in the molecule of hydrogen donor monomers: there are 12 hydrogen atoms in the TGM-3 molecule and 4 atoms in the DMEG molecule. The hydrogen atoms of the $-O-CH_2-$ moiety alone are taken into account, since they are the most reactive [23]. Similar trends were observed in the photoreduction of PQ in the presence of DMEG and TGM-3 (molar ratio, 1 : 50) in a vacuum [19] or in the presence of polymethylbenzenes [22]. As the concentration of the monomers increases, the threefold difference in the number of hydrogen atoms between DMEG and TGM-3 is leveled and the values of k_H in the monomer media become identical.

Compared with DMEG and TGM-3, the photoreduction of PQ in the presence of OKM-2 is slower, although there are 16 hydrogen atoms in the $-O-CH_2-$ moiety of the OKM-2 molecule. The reason behind such anomalous behavior of OKM-2 can be the formation of relatively stable associates by OKM-2 molecules [24, 25], for example, through hydrogen bonding between the oxygen atoms of the carbonate groups of one molecule and the methylene units of the other. This association should lead to a decrease in the number of $-CH_2-$ groups available for attacking by the photoexcited PQ molecule and, hence, to a decrease in k_H.

Illumination with visible light of porous polymer samples impregnated with a PQ solution of the immersion liquid (mixture of benzene and 1,2-dichlorobenzene) leads to discoloration of the samples. Figure 3 shows the changes, caused by irradiation with visible light, in the spectral characteristics of a 2-mm thick porous polyDMEG sample impregnated with a PQ solution in the benzene—1,2-dichlorobenzene solvent blend. In this experiment (unlike the case of solutions of PQ and monomers in benzene), the networked polymer of the pore surface acts as a hydrogen donor for the photoexcited PQ molecule. The change in the PQ concentration with time during irradiation
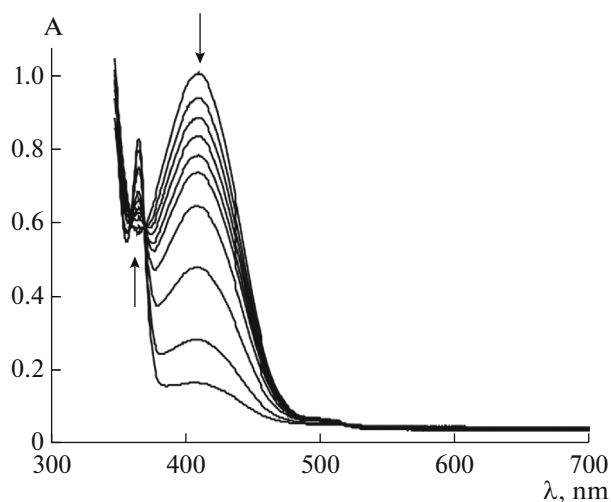

Fig. 2. Spectral changes caused by irradiation of a solution of 9,10-phenanthrenequinone (6.8×10^{-4} mol/L) and ethylene glycol dimethacrylate (6.8×10^{-1} mol/L) in benzene; irradiation time (spectra from top to bottom): 0, 10, 20, 30, 40, 50, 70, 120, 200, and 290 s; visible light; air; 298 K.

of the porous polymer is also described by the first-order rate law.

To reveal the effect of the nature of the polymer chain and the characteristics of porous polymers on

Table 1. Influence of the DMEG, TGM-3, and OKM-2 concentration in benzene on the photoreduction kinetics of 9,10-phenanthrenequinone (6.8×10^{-4} mol/L) and the k_H value for the photoreduction of 9,10-phenanthrenequinone in the pure monomers

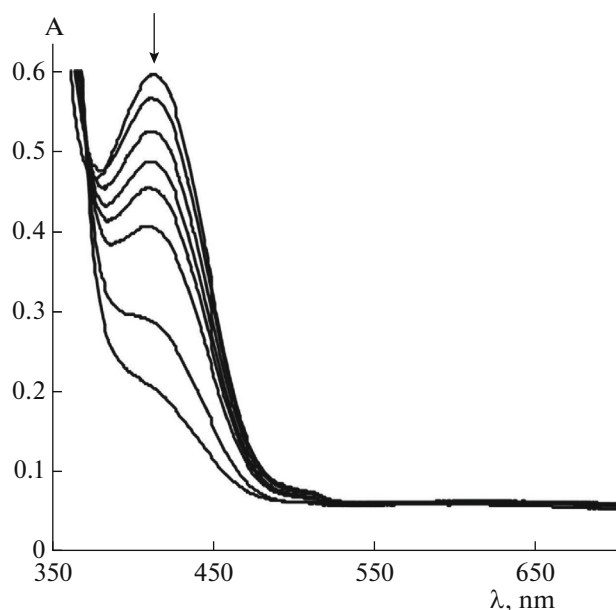| No.	Monomer	[PQ] : [monomer]	$k_H \times 10^3 \text{ s}^{-1}$
1	DMEG	1 : 10	0.45
2		1 : 500	2.5
3		1 : 1000	2.7
4		In monomer	
5	TGM-3	1 : 10	1.3
6		1 : 100	2.5
7		1 : 250	3.1
8		1 : 500	4.2
9		1 : 1000	3.8
10		In monomer	4.0
11	OKM-2	1 : 10	0.4
12		1 : 50	0.55
13		1 : 100	0.85
14		1 : 250	1.2
15		1 : 500	1.5
16		1 : 1000	1.7
17		In monomer	2.2

Fig. 3. Spectral changes caused by irradiation of a porous sample of polyDMEG (thickness 2 mm) in a 9,10-phenanthrenequinone solution in 60 : 40 (v/v) benzene−1,2-dichlorobenzene mixture. Irradiation time (spectra from top to bottom): 0, 30, 60, 90, 120, 240, 540, and 1140 s; visible light; air; 298 K.

k_H, various porous polymer matrices synthesized from DMEG, TGM-3, and OKM-2 were used, with the pore size varying from tens to hundreds of nanometers. Typical AFM images of the surface of the investigated porous polymer blocks are presented for the polyD-MEG samples as an example (Fig. 4).

Table 2 lists some characteristics of the porous polymers produced from DMEG, TGM-3, and OKM-2 and the values of k_H (in the photoreduction of PQ in 1,2-dichlorobenzene, $k_H = 0.1 \times 10^{-3}$ s^{-1}).

These data show that k_H does not depend on the nature of the repeat unit of a pore-wall polymer. In the

Table 2. Characterization of porous matrices: pore size (d) range, specific surface area (S_{sp}) of pores, sorption of immersion liquid N by porous polymers, and rate constant (k_H) for 9,10-phenanthrenequinone photoreduction in porous polymers impregnated with the immersion liquid

No.	Porous matrix	d, nm	S, m^2/g	$k_H \times 10^3$ s^{-1}
1	polyDMEG	30−100	250	1.1
2	polyTGM-3	30−150	75	1.3
3	polyTGM-3	50−200	70	1.1
4	polyDMEG	150−400	65	1.0
5	polyOKM-2	200−500	41	1.2
6	polyDMEG	50−300	38	1.1
7	polyOKM-2	100−300	24	1.4

polyDMEG pores, $k_H = 1.1$, 1.0, or 1.1×10^3 s^{-1} (samples 1, 4, 6); in the polyTGM-3 pores, $k_H = 1.6$ or 1.1×10^3 s^{-1} (samples 2, 3); and in the polyOKM-2 pores, $k_H = 1.2$ or 1.4×10^3 s^{-1} (samples 5, 7). This behavior indicates that, unlike the case of liquid monomers or their solutions, the availability of the −CH$_2$− groups of all the three monomers is the same on the pore surface. From the data of Table 2 it also follows that an increase in the pore size from tens to hundreds of nanometers and the corresponding decrease by an order of magnitude of the specific surface area of the pores from 250 to 24 m^2/g almost do not affect the value of k_H. The reason for the observed effect can be as follows. The lifetime of the excited triplet state of PQ is $\tau \sim 5 \times 10^{-4}$ s [20]. During this time, the molecule must be able to encounter a hydrogen donor molecule and react with it. The average displacement of the 9,10-phenanthrenequinone molecule Δ over a time τ can be estimated from the Einstein−Smoluchowski equation:

$$\Delta = (2D\tau)^{0.5},$$

where D is the diffusion coefficient of the quinone molecule in the solvent. If we take that D of 9,10-phenanthrenequinone is 1.5×10^{-5} cm^2/s (according to [26], $D = 1.25 \times 10^{-5}$, 1.19×10^{-5}, and 1.68×10^{-5} cm^2/s for dibromonaphthalene, naphthalene, and quinone, respectively, in benzene at $T = 288$ K and $D = 0.95 \times 10^{-5}$ cm^2/s for phenanthrene at $T = 281$ K), then $\Delta = 1200$ nm. This means that in pores of ~100 nm in size, all photoexcited PQ molecules manage to reach the pore wall and enter the photoreduction reaction during the excited-state lifetime. Accordingly, the pore size in the range from tens to hundreds of nanometers should have no effect on the PQ photoreduction kinetics, which is indeed the case observed in the experiment.

Thus, the dimethacrylate monomers DMEG, TGM-3, OKM-2 and porous polymers on their basis are hydrogen donors for the photoexcited 9,10-phenanthrenequinone molecule. The effective rate constant for the photoreduction of 9,10-phenanthrenequinone in the pores is two−four times less than in the monomer media. For the series of the porous polymers examined, it does not depend on the monomer nature and remains constant when the pore size varies from tens to hundreds of nanometers, a property that can be useful for postmodification of a porous polymer by photoinduced grafting.
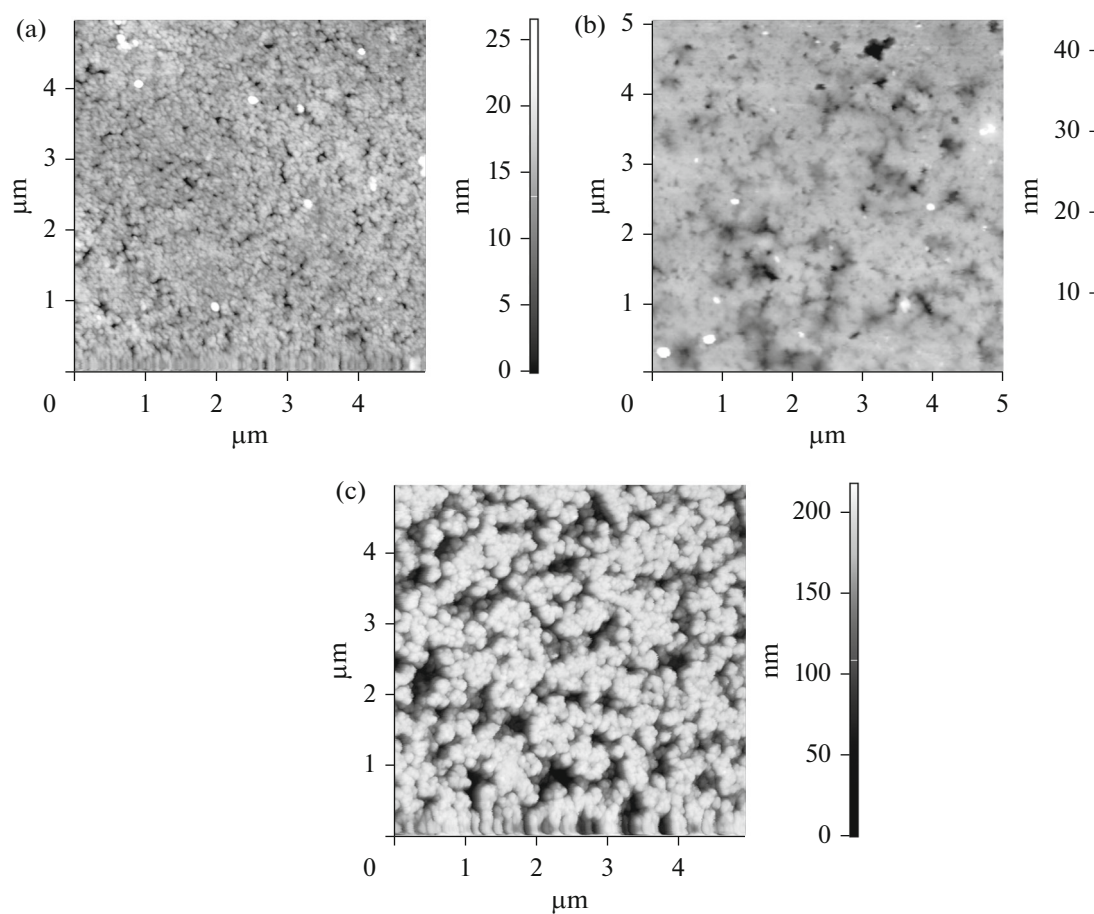
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Fig. 4. AFM images of the surfaces of porous polyDMEG blocks with different pore sizes: (a) homogeneous porous structure with pores of a 30 to 100 nm size, (b) single pores of 50−300 nm in size are observed on the surface, and (c) a homogeneous porous structure with the minimum pore size not exceeding 150 nm and the largest pore size of 400 nm.

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