# Influence of *o*-benzoquinone nature on initiation of radical polymerization by the *o*-benzoquinone—*tert*-amine system

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*o*-Benzoquinones initiate radical polymerization of methacrylates under visible light irradiation in the presence of tertiary amines. Spectral sensitivity of the initiating system coincides with absorption bands of *o*-benzoquinone attributed to the $S(\pi\to\pi^*)$ ($\lambda_{max} \approx 400$ nm) and $S(n\to\pi^*)$ ($\lambda_{max} \approx 600$ nm) transitions. The amine radicals (Am$^\cdot$) initiating polymerization are generated by the photoreduction of Q in the presence of AmH from the triplet radical pair $^3$(QH$^\cdot$, Am$^\cdot$). The yield of Am$^\cdot$ depends on the difference between the volumes of substituents in the 3 and 6 positions of the quinoid ring and is maximal for symmetrically substituted *o*-benzoquinones. For a series of derivatives of symmetrical 3,6-di-*tert*-butyl-*o*-benzoquinone, the rate of photopolymerization of α,ω-bis(methacryloyloxyethyleneoxycarbonyloxy)ethyleneoxyethylene (OCM-2) in the presence of *N*,*N*-dimethylaniline is determined by the free energy ($\Delta G_e$) of electron transfer from the amine to photoexcited *o*-benzoquinone. The $\Delta G_e$ value includes the energies of oxidation of the amines and reduction of the *o*-quinones and the energy of the 0→0 transition of the triplet excited state of *o*-benzoquinones, which are equal to their redox potentials. The photopolymerization rate is maximal for $\Delta G_e \approx 0$.

**Key words:** *o*-benzoquinones, *N*,*N*-dimethylaniline, photopolymerization, free energy of electron transfer.

Arylketones and quinones with the lowest excited state $T(n\to\pi^*)$ are highly reactive in the elimination of the hydrogen atom from H-donating compounds.[1] The radical formed by dehydrogenation adds to unsaturated compounds and can initiate their radical polymerization. These reactions provide the basis for the photoinitiation of polymerization by benzophenone and its derivatives, *p*- and *o*-quinones with the fused aromatic system (*viz.*, naphthoquinones, anthraquinones, 9,10-phenanthrenequinone), and camphorquinone.[2—4] It has previously[5] been reported that *o*-benzoquinone derivatives (Q) in combination with tertiary amines (AmH) also initiate polymerization of the methacrylate monomers and oligoacrylates by the visible light. However, no systematic studies of the influence of *o*-benzoquinones on photopolymerization have been conducted.

In this work, we studied the mechanism of formation of radicals by photoreduction of *o*-benzoquinones in the presence of tertiary amines.

## Experimental

Electronic absorption spectra were measured on Specord M-40 and SF-14 spectrophotometers in toluene. Potentials of the half-wave of the reversible one-electron reduction $E(\mathrm{Q}^{\cdot-}/\mathrm{Q})$ of *o*-benzoquinones were determined in DMF against the saturated calomel electrode.

Commercial oligodimethacrylates, *viz.*, α,ω-bis(methacryloyloxyethyleneoxycarbonyloxy)ethyleneoxyethylene (OCM-2) and ethylene glycol dimethacrylate (DMEG) were purified according to standard procedures.[6]

The photopolymerizing mixture was prepared by dissolving of *o*-benzoquinone ([Q] = $2.9 \cdot 10^{-3}$ mol L$^{-1}$) and amine ([AmH] = $2.9 \cdot 10^{-1}$ mol L$^{-1}$) in OCM-2. The solution was introduced into glass ampules ~3 mm in diameter and degassed. The photopolymerization kinetics was studied by the thermographic method.[7] A KGM-24-150 lamp with a focuser was used as a light source. The required spectral range was separated from the full luminous flux of the lamp by glass light filters SS-4 ($\lambda < 450$ nm), ZhS-16 ($\lambda > 500$ nm), and KS-17 ($\lambda > 650$ nm). The distance between the focuser and ampule in the thermographic installation was 80 cm. An ampule filled with the mixture that has been polymerized was used as a reference. The degrees of conversion of OCM-2 were calculated from the thermographic curves, and the kinetic curves of polymerization were plotted. The theoretical value of the photopolymerization heat (56 kJ mol$^{-1}$) was used in calculations. The maximum photopolymerization rate ($W_{max}$) was calculated from the slope of the kinetic curve.

Polarography of solutions of *o*-quinones in DMF ($5 \cdot 10^{-3}$ mol L$^{-1}$) was studied against the background of 0.1 *M* NaClO$_4$ using a PU-1 polarograph. The supporting salt was doubly recrystallized from bidistillated water and dried *in vacuo* for 12 h at 100 °C. DMF was distilled at 5—10 Torr, stored for ~24 h with molecular sieves 4A, and then distilled at 2 Torr in an Ar flow.

Solvents were purified by standard procedures.[8] *N*,*N*-Dimethylaniline (**1**) (Aldrich) was purified by distillation. *o*-Benzoquinones were synthesized by previously described methods.[9—11]

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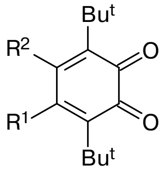
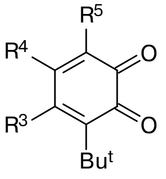
## Results and Discussion

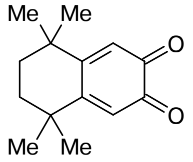
Two series of sterically hindered *o*-benzoquinones were chosen in the study. The first series was comprised of the 3,6-di-*tert*-butylbenzoquinone-1,2 derivatives (**2a—i**) with different substituents in positions 4 and 5 of the quinoid ring. The second series involved the 3-*tert*-butylbenzoquinone-1,2 derivatives (**3a—c**). In addition, 5,5,8,8-tetramethyltetrahydroquinone-2,3 (**4**) was used.



**2a—i**



**3a—c**



**4**

**2:** $R^1$ = H, $R^2$ = Pr$^i$ (**a**), Pr$^n$ (**b**), Ph (**c**), H (**d**), Cl (**e**), F (**f**), $NO_2$ (**h**), CN (**i**); $R^1$ = $R^2$ = F (**g**)
**3:** $R^3$ = H, $R^4$ = Bu$^t$, $R^5$ = H (**a**); $R^3$ = H, $R^4$ = H, $R^5$ = Me (**b**), Pr$^i$ (**c**)

Photopolymerization was conducted in the presence of *N*,*N*-dimethylaniline (**1**) and 1-dimethylaminopropan-2-ol $Me_2NCH_2CH(OH)Me$ (**5**).

To reveal the mechanism of formation of radicals initiating polymerization, we studied the region of spectral sensitivity of the Q—AmH photoinitiating system, the spectral characteristics of *o*-benzoquinones, and the influence of the nature of *o*-benzoquinone on the photopolymerization rate.

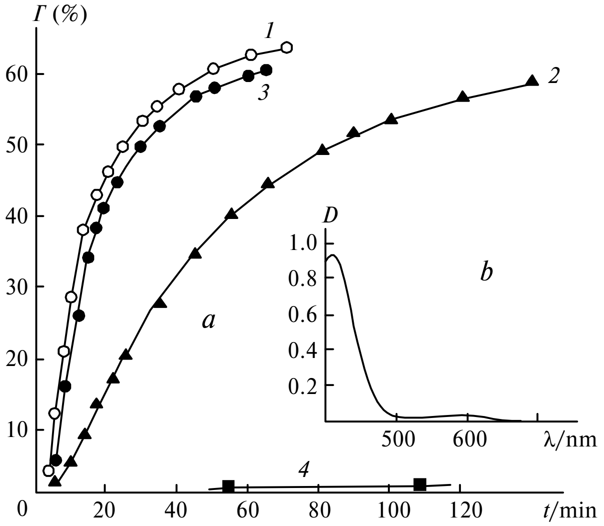


**Fig. 1.** *a*. Kinetic curves for photopolymerization of OCM-2—DMEG (weight ratio 9 : 1) in the presence of **2d—5** obtained by exposure with the full light of a KGM 24-150 lamp (*1*) and light with λ < 450 nm (*2*), > 500 nm (*3*), and > 650 nm (*4*). *b*. Electronic absorption spectrum of *o*-benzoquinone **2d** in toluene.

It is seen from the obtained kinetic curves (Fig. 1) that the photopolymerization of a mixture of OCM-2 with DMEG is initiated by the visible light in the spectral range from 400 to 650 nm. Comparison of the kinetic curve of photopolymerization under the full light of the lamp (see Fig. 1, curve *1*) with the curves describing the process initiated by the light with λ < 450 nm, λ > 500 nm, and λ > 650 nm (curves *2*, *3*, and *4*, respectively) shows that the maximum of sensitivity to the emission from a halogen incandescent lamp lies in a region of 500—650 nm. Amine **5** used in experiments is a colorless substance and does not form noticeable amounts of a charge-transfer complex (CTC) with compound **2d**. Therefore, the photosensitivity of the system in the visible region is determined only by the absorption of the actinic light by *o*-orthobenzoquinone. Comparison of the spectral sensitivity of the **2d—5** system and positions of the absorption bands of *o*-benzoquinones in

**Table 1.** Positions of maxima of absorption bands (λ) in the visible region (toluene), reduction potentials (*E*) of *o*-benzoquinones **2a—i** and compounds **3a—c** and **4** and the maximal ($W_{max}$) and normalized ($W_n$) photopolymerization rates of OCM-2 in the presence of the Q—**1** system*

| *o*-Benzoquinone | $R^3$ | $R^4$ | $R^5$ | $R^6$ | $\lambda_{\pi\pi^*}$ (ε) | $\lambda_{n\pi^*}$ (ε) | $-E(Q^{\cdot -}/Q)$ /V | $W_{max}$ /min$^{-1}$ | $W_n$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | nm | | | | |
| **2a** | Bu$^t$ | Pr$^i$ | H | Bu$^t$ | 400 | 578 (130) | 0.53 | 1.7 | 0.22 |
| **2b** | Bu$^t$ | Pr$^n$ | H | Bu$^t$ | 404 (2100) | 578 (76) | 0.51 | 3.0 | 0.68 |
| **2c** | Bu$^t$ | Ph | H | Bu$^t$ | 412 (2200) | 595 (97) | 0.41 | 3.2 | 0.92 |
| **2d** | Bu$^t$ | H | H | Bu$^t$ | 410 (2400) | 598 (60) | 0.39 | 3.5 | 1.00 |
| **2e** | Bu$^t$ | Cl | H | Bu$^t$ | 398 (2150) | 575 (86) | 0.37 | 2.7 | 0.77 |
| **2f** | Bu$^t$ | F | H | Bu$^t$ | 398 (2300) | 566 (60) | 0.34 | 2.6 | 0.74 |
| **2g** | Bu$^t$ | F | F | Bu$^t$ | 387 (2200) | 535 (66) | 0.34 | 2.0 | 0.52 |
| **2h** | Bu$^t$ | $NO_2$ | H | Bu$^t$ | 388 (2800) | 592 (56) | 0.10 | 1.1 | 0.37 |
| **2i** | Bu$^t$ | CN | H | Bu$^t$ | 388 (2500) | 591 (58) | 0.06 | 0.3 | 0.09 |
| **3a** | Bu$^t$ | H | Bu$^t$ | H | 400 | 595 (40) | 0.37 | 0.4 | 0.17 |
| **3b** | Bu$^t$ | H | H | Me | 400 | 583 (53) | 0.35 | 1.0 | 0.32 |
| **3c** | Bu$^t$ | H | H | Pr$^i$ | 417 (2200) | 595 (26) | 0.35 | 1.5 | 0.50 |
| **4** | H | $Me_2C(CH_2)_2CMe_2$ | | H | 415 (950) | 595 (20) | 0.27 | 3.0 | 2.57 |

* Spectral characteristics and $E(Q^{\cdot -}/Q)$ values for compounds **2a,b,d—i**.[10]

the visible region, which correspond to the S($\pi\to\pi^*$) and S($n\to\pi^*$) electronic transitions of the carbonyl groups (Table 1) shows that both absorption bands of *o*-benzoquinones are photochemically active in the photoinitiation of polymerization. This is associated with the fact that in the elimination of the H atom by carbonyl-containing compounds the lowest excited state T($n\to\pi^*$) is active, and the *o*-benzoquinone molecule transforms into this state from both the S($\pi\to\pi^*$) and S($n\to\pi^*$) states.[10,12]

In order to simplify calculations, we studied the reaction under irradiation corresponding to the S($n\to\pi^*$) transition. As can be seen from the data in Table 1, the absorption bands of the S($n\to\pi^*$) transition of all studied quinones **2a**—**i**, **3a**—**c**, and **4** lie in the same spectral region of 535 nm < $\lambda_{max}$ < 598 nm. Therefore, the photopolymerization kinetics of all *o*-benzoquinones can be studied using one source of polychromatic radiation, separating the radiation with $\lambda \geq 500$ nm from the full light. The initiation rate of photopolymerization is proportional to the molar absorption coefficient of quinone at the operating wavelength. Hence, Table 1 contains, along with the experimental $W_{max}$ values for each quinone, the calculated values of the photopolymerization rate normalized to the molar absorption coefficient and to $W_{max}$ for quinone **2d**.

As can be seen from these data, the nature of *o*-benzoquinone has a strong effect on the photopolymerization rate. *o*-Benzoquinones **2a**—**i** are numerated in the order of increasing the electron-withdrawing ability, which can numerically be estimated by the electrochemical reduction potential $E(Q^{\cdot -}/Q)$. In the series of 3,6-di-*tert*-butylbenzoquinone-1,2 derivatives on going from **2a** to **2i**, the $E(Q^{\cdot -}/Q)$ values increase monotonically from −0.54 to −0.06 V, and the photopolymerization rate changes extremely and is maximal for quinone **2d**. With the purpose for explaining this effect, we compared the rates of photopolymerization and photoreduction of *o*-benzoquinones. As can be seen in Fig. 2, the normalized rate constants of photoreduction ($k_n$) for *o*-benzoquinones are also characterized by extreme plots *vs.* $E(Q^{\cdot -}/Q)$. As a whole, the plots of $k_n$ and $W_n$ *vs.* $E(Q^{\cdot -}/Q)$ of *o*-benzoquinones coincide to a great extent. This indicates that the photopolymerization rate in the presence of compounds **2a**—**i** is determined first of all by the photoreduction of *o*-benzoquinone.

It has previously[10] been shown that in the general case $k_n$ exhibits an extreme dependence not simply on $E(Q^{\cdot -}/Q)$ but on the free energy of electron transfer from the amine molecule to the photoexcited molecule of *o*-benzoquinone ($\Delta G_{e,t}$),[13] and the analytical expression for the calculation of this energy contains $E(Q^{\cdot -}/Q)$:

$$\Delta G_{e,t} = -\Delta E_{00} - E(Q^{\cdot -}/Q) + E(AmH/AmH^{\cdot +}) + 0.36\ (eV), \qquad (1)$$

where $\Delta E_{00}$ is the energy of the triplet 0→0 transition of the lowest excited state of the photoacceptor (in this case, *o*-benzoquinone); $E(Q^{\cdot -}/Q)$ and $E(AmH/AmH^{\cdot +})$ are the energies of reduction of the acceptor (*o*-benzoquinone) and oxidation of donor **1**, which are numerically equal to the electrochemical potentials of the acceptor (*o*-benzoquinone) and donor **1**, respectively. For compounds **2a**—**i** $\Delta E_{00} \approx 1.35$ eV,[10] and the electrochemical potential of oxidation of **1** is 0.71 V.[14] The calculation of $\Delta G_{e,t}$ for each **2a**—**i** pair and **1** allowed us to consider the change in $k_n$ and $W_n$ with variation of $\Delta G_{e,t}$ (see Fig. 2). The maxima of $k_n$ and $W_n$ are observed at $\Delta G_{e,t} \approx 0.1$ eV.

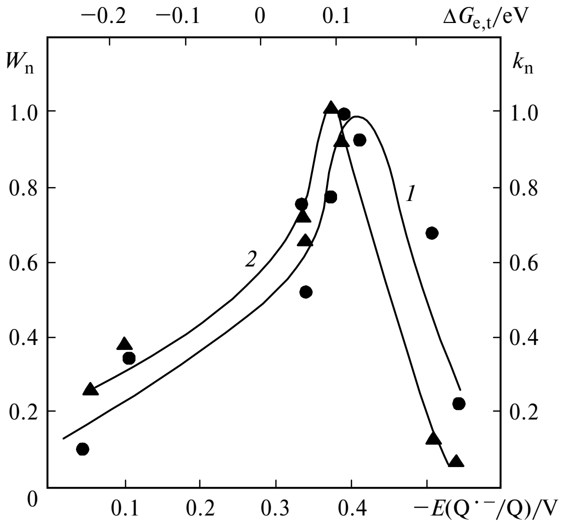


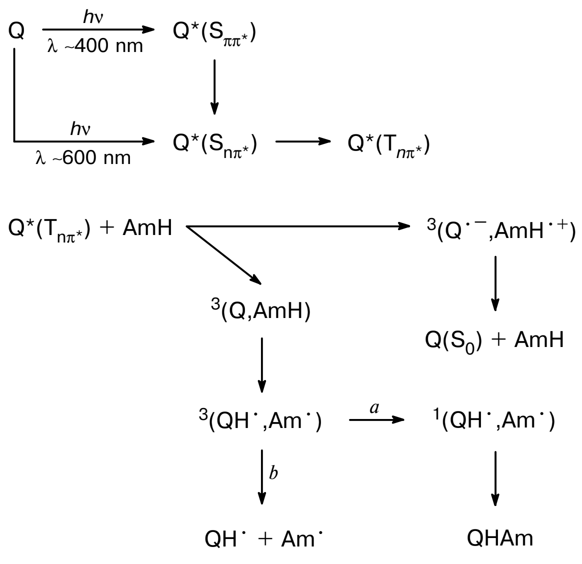
**Fig. 2.** Plots of the normalized photopolymerization rate $W_n$ (*1*) of OCM-2 in the presence of the (**2a**—**i**)—**1** system and normalized rate constant of photoreduction $k_n$ (*2*) of **2a**,**b**,**d**—**i** in the presence of **1** in toluene *vs.* electrochemical potential of *o*-benzoquinones $E(Q^{\cdot -}/Q)$ and free energy of electron transfer $\Delta G_{e,t}$ calculated for the (**2a**—**i**)—**1** pair. For clarity the $k_n$ values were normalized to the $k_n$ value for **2d**. Data on the photoreduction of **2a**,**b**,**d**—**i** were taken from Ref. 10.

Thus, Eq. (1) describes the dependence of the photopolymerization rate in the presence of the Q—AmH system on the energy of the *o*-benzoquinone photoexcited state and the ratio of the redox potentials of quinone and amine. The photopolymerization rate is maximal at $\Delta G_{e,t} \approx 0$ and decreases as $\Delta G_{e,t}$ changes from zero to the positive or negative values. This approach explains why, unlike other quinones (9,10-phenanthrenequinone, camphorquinone), *o*-benzoquinones initiate polymerization only in the presence of tertiary amines acting as coinitiators of photopolymerization. The calculation of $\Delta G_{e,t}$ using Eq. (1) shows that donors with the $E(AmH/AmH^{\cdot +})$ values from +0.56 to +1.03 V are appropriate for quinones **2a**—**i**. This interval of oxidation potentials is characteristic of precisely tertiary amines, for example, compound **1** and its derivatives.[14] As compared to *o*-benzoquinones, $\Delta E_{00}$ of other quinones are much higher, for example, for 9,10-phenanthrene $\Delta E_{00} \approx 2.0$ eV [12] at approximately the same potential $E(Q^{\cdot -}/Q) \approx -0.3$ V.[14] Therefore, the acceptor ability of the photoexcited 9,10-phenanthrenequinone molecule is sufficient for the detachment of the H atom from molecules of the monomer or solvent and for the initiation of polymerization without additives of the coinitiator.[2,3]

However, Eq. (1), which describes the observed dependence for the series of 3,6-di-*tert*-butylbenzoquinone-1,2 derivatives, is not fulfilled on going to *o*-benzoquinones with different structures. For example, it does not explain the distinctions in the photoinitiating ability of *o*-benzoquinones **2d** and **3a**. At almost the same reduction potential ($-0.39$ and $-0.37$ V, respectively), the photopolymerization rates differ by more than 5 times (see Table 1), and quinone **3a** is photoreduced twofold more rapidly than **2d**. To explain this effect, we analyzed the photoreduction products of **2d** and **3a** in the presence of *p*-bromo-*N*,*N*-dimethylaniline.[15]

*o*-Benzoquinone **2d** is quantitatively reduced to the corresponding pyrocatechol, whereas the photoreduction of compound **3a** affords a mixture of products, the main of which is 2-(*N*-*p*-bromophenyl-*N*-methylaminomethoxy)-4,6-di-*tert*-butylphenol. The formation of different products indicates that, depending on the structure of *o*-benzoquinone, two routes of photoreduction are possible, only one of which results in free radicals capable of initiating polymerization. We assume that the reaction occurs according to Scheme 1. At the first step, the *o*-benzoquinone molecule is excited to the lowest excited triplet state. The interaction of the photoexcited *o*-benzoquinone molecule with the amine molecule occurs *via* two routes. The first of them (*a*) is the outersphere electron transfer resulting in the generation of the (QH$^{\bullet -}$, Am$^{\bullet +}$) radical ion pair, which then is deactivated to the initial compounds in the ground state. In this case, a proton is not transferred and *o*-benzoquinone is not reduced. The second route (*b*) is the formation of the triplet exciplex[10] $^3$(Q, AmH) or (as formulated by Kochi[16,17]) "encounter complex." This is precisely the complex in which the transfer of the H atom occurs, and the triplet ion radical pair $^3$(QH$^\bullet$, Am$^\bullet$) is generated. The photoreduction resulting in radical or non-radical products through the formation of the $^3$(Q, AmH) intermediate complex and the electron transfer are parallel. This assertion is based on the following. The dependence of $W_n$ on $\Delta G_{e,t}$ found in this work and previously established functions of $\Delta G_{e,t}$ for the photoreduction rate constants of *o*-benzoquinones[10] and fluorenone[18] in the presence of derivatives of compound **1** virtually coincide with the plot of the equilibrium constant of formation of the triplet exciplex in the *p*-benzoquinone—polyalkylbenzene[17] system *vs.* $\Delta G_{e,t}$. All of them are extremal and have a maximum at $\Delta G_{e,t} \approx 0$. At the same time, the plot of the electron transfer rate constant *vs.* $\Delta G_{e,t}$ is not extremal: a monotonic increase is observed with the transition of $\Delta G_{e,t}$ to the region of negative values until the diffusional limit is reached.[3,17]

**Scheme 1**



The triplet radical pair formed due to the transfer of the H atom in the triplet exciplex can be transformed into the singlet pair followed by radical recombination in the solvent "cage." In this case, *o*-benzoquinone is reduced but the free radicals do not escape to the reaction medium. The reaction product is the corresponding ester. If the lifetime of the triplet radical pair is rather long for it to decompose and for its radicals QH$^\bullet$ and Am$^\bullet$ to escape from the solvent "cage," the products of their independent transformations are formed. The QH$^\bullet$ radicals enter into the disproportionation reaction to give pyrocatechol and quinone, and Am$^\bullet$ can initiate radical polymerization.

Our data indicate that the direction of the triplet radical pair evolution is determined by the molecular structure of *o*-benzoquinone. *o*-Benzoquinones **2d** and **3a** differ by the positions of substituents relatively to the carbonyl groups of *o*-benzoquinone. In molecule **2d** the *tert*-butyl groups are arranged symmetrically in positions 3 and 6 of the quinoid ring: route (*b*) takes place during photoreduction (see Scheme 1), and photopolymerization occurs with a high rate. Quinone **3a** also has the bulky *tert*-butyl group in position 3 but the H atom is present in position 6, and photoreduction proceeds mainly *via* route (*a*), and the photopolymerization rate is fivefold lower than that for **2d**. To estimate the influence of volume of substituents on the efficiency of *o*-benzoquinones as photoinitiators for the series of 3-*tert*-butylbenzoquinone-1,2 derivatives, we studied changes in the photopolymerization rates with a successive decrease in the size of the substituent in position 6. As can be seen in the plot of $W_n$ *vs.* difference of steric constants $\Delta(-E^\circ_s)$[19] (Fig. 3) of the substituents in positions 3 and 6 of the quinoine ring, the photopolymerization rate is proportional to $-\Delta(-E^\circ_s)$: the lower the difference in steric constants, the higher $W_n$. It could be assumed that the observed effect is related to a change in screening of the radical center in

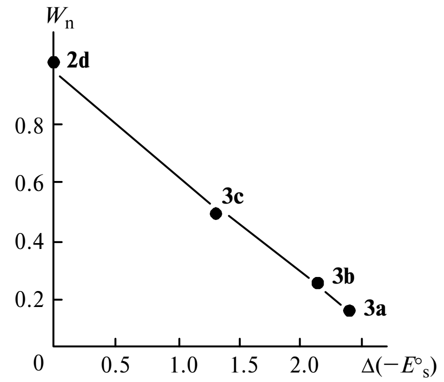
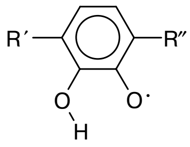


**Fig. 3.** Plot of the photopolymerization rate $W_n$ of OCM-2 in the presence of the (**2d**,**3a**—**c**)—**1** initiating system *vs.* difference of the Palm steric constants $\Delta(-E°_s)$ of substituents in positions 3 and 6 of the quinone ring.

the series of *o*-benzosemiquinones QH$^•$. The QH$^•$ radical of *o*-benzoquinone **2d** exhibits the efficient steric screening of the radical center by the *tert*-butyl substituents. This could impede radical recombination in the (QH$^•$, Am$^•$) radical pair and, hence, favor the escape of the radicals from the cage resulting in an increase in $W_n$. When one *tert*-butyl group is replaced by a less bulky substituent, the screening effect decreases, the probability of radical recombination should increase, and $W_n$ should decrease. However, in this case, the minimal photopolymerization rate is expected for compound **4**, whose substituents in positions 3 and 6 are the H atoms and screening of the semiquinone center is absent in QH$^•$. Nevertheless, *o*-benzoquinone **4** is the most efficient photoinitiator of polymerization of all *o*-benzoquinones studied (see Table 1). Therefore, the direction of the triplet radical pair evolution is not controlled by screening. *o*-Benzoquinone **4**, similarly to quinone **2d**, has the same substituents in positions 3 and 6. It is most likely that the difference in volumes of the substituents in positions 3 and 6 of the aromatic ring of the QH$^•$ semiquinone radical or, in other words, the symmetric character of QH$^•$ has a critical influence on the stability of the triplet radical pair $^3$(QH$^•$,Am$^•$). With a decrease in the difference in volumes of the substituents (or with an enhancement of the symmetric character of the semiquinone radical), the stability of the triplet radical pair increases. The mechanism of this effect is yet unclear.



QH$^•$

Thus, the efficiency of *o*-benzoquinones in the photoinitiation of polymerization by the Q—AmH system is determined by the energy and structural parameters of *o*-benzoquinone. The electron-withdrawing ability of *o*-benzoquinone and the energy of the photoexcited triplet state along with the electron-donating properties of amine specify the photoreduction rate of *o*-benzoquinone, thus determining the general efficiency of formation of the intermediate radical products. The molecular structure of *o*-benzoquinone pre-determines the ratio between two routes of photoreduction: first, the generation of free radicals capable of initiating polymerization into the reaction medium and second, radical recombination in the solvent (monomer) "cage" to form compounds inactive in the initiation of polymerization. The most efficient initiators are *o*-benzoquinones with symmetrical substituents in positions 3 and 6 of the quinone ring in pair with tertiary amines when the free energy of electron transfer from the amine molecule to the photoexcited *o*-benzoquinone molecule is $\Delta G_{e,t} \approx 0$.

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