Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Photooxidation-Reduction Sensitized by Copolymers of [2-(9,10-Anthraquinonyl) methyl Methacrylate. II. Intramolecular Chemical Quenching by 2-Hydroxyethyl Methacrylate Units

Takayuki Nakahira[a]; Hirofumi Maruyama[a]; Susumu Iwabuchi[a]; Kuniharu Kojima[a]
[a] Department of Applied Chemistry, Faculty of Engineering Chiba University Yayoi-cho 1, Chiba, Japan

To cite this Article Nakahira, Takayuki , Maruyama, Hirofumi , Iwabuchi, Susumu and Kojima, Kuniharu(1980) 'Photooxidation-Reduction Sensitized by Copolymers of [2-(9,10-Anthraquinonyl) methyl Methacrylate. II. Intramolecular Chemical Quenching by 2-Hydroxyethyl Methacrylate Units', Journal of Macromolecular Science, Part A, 14: 5, 779 — 789

To link to this Article: DOI: 10.1080/00222338008066648

URL: http://dx.doi.org/10.1080/00222338008066648

J. MACROMOL. SCI.--CHEM., A14(5), pp. 779-789 (1980)

Photooxidation-Reduction Sensitized by Copolymers of [2-(9,10-Anthraquinonyl)] methyl Methacrylate. II. Intramolecular Chemical Quenching by 2-Hydroxyethyl Methacrylate Units*

TAKAYUKI NAKAHIRA, HIROFUMI MARUYAMA, SUSUMU IWABUCHI, and KUNIHARU KOJIMA

Department of Applied Chemistry
Faculty of Engineering
Chiba University
Yayoi-cho 1, Chiba 260, Japan

ABSTRACT

Copolymers of [2-(9,10-anthraquinonyl)]methyl methacrylate (AQMMA) with 2-hydroxyethyl methacrylate(HEMA) were prepared, and their photosensitizing efficiencies were examined with respect to oxidation-reduction between L-ascorbic acid and Fast Red A in dimethylformamide. The photosensitizing efficiency was found to decrease with increasing HEMA content in the polymer. Intramolecular chemical quenching of anthraquinone triplet by HEMA units leading to the formation of O-alkylated anthrahydroquinone derivatives (photoadducts) was found to be responsible for the observed decrease in photosensitizing efficiency. The linear relationship between the quantum yield ratio of photoadduct formation to photosensitization and the mole ratio of HEMA to AQMMA suggests that triplet energy delocalization is effected in the AQMMA sequence where the initial excitation takes

---

*For Part I see T. Nakahira, E. Shinimiya, T. Fukumoto, S. Iwabuchi, and K. Kojima, Eur. Polym. J., 14, 317 (1978).

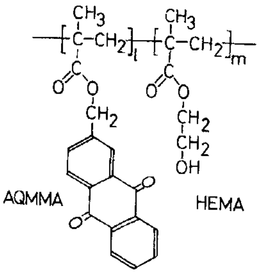
place and that the HEMA sequences nearest to the AQMMA sequence are involved in photoadduct formation.

INTRODUCTION

In designing functional polymers such as polymeric catalysts, understanding of the interactions among functional groups in polymeric systems is extremely important; so-called polymer effects are to be interpreted in terms of intra- and/or intermolecular interactions which are unique to polymeric systems and absent in low molecular systems. Excimer formation and excitation energy migration along the polymer chain are known to occur between nearest-neighbor or nonnearest-neighbor chromophores in polymers having pendant aromatic groups [1-5].

We have been engaged in studying polymers capable of sensitizing photooxidation-reduction [6-8]. Among those studied are copolymers of [2-(9,10-anthraquinonyl)]methyl methacrylate(AQMMA) and 2-naphthylmethyl methacrylate for oxidation-reduction between Fast Red A and L-ascorbic acid [8]. We observed, in addition to intramolecular quenching of the anthrquinone triplet by the naphthalene unit, chemical quenching leading to the formation of O-alkylated derivatives of anthrahydroquinone not capable of reducing Fast Red A, though its extent was not large at the initial stage of irradiation.

In the present study, we prepared yet another type of AQMMA copolymer, using 2-hydroxyethyl methacrylate(HEMA) as a comonomer, and examined more closely the intramolecular chemical quenching in photosensitization of oxidation-reduction by the anthraquinone unit.



EXPERIMENTAL

AQMMA was prepared as described previously [8]. Commercial HEMA was purified by distillation under reduced pressure. Copolymerization was carried out in dimethylformamide at 60°C with azobisisobutyronitrile as an initiator. Polymers were precipitated in diethyl ether, reprecipitated several times from dimethylformamide/ diethyl ether, washed thoroughly with diethyl ether, and dried in vacuo. Viscosity measurements were performed in dimethylformamide at 30° C. Absorption of the anthraquinone unit at 330 nm was used to determine its content in the polymer. The mean sequence lengths of AQMMA and HEMA residues were estimated from the initial monomer concentrations and the monomer reactivity ratios obtained by the Mayo-Lewis equation; r_1 (AQMMA) = 0.05 and r_2 (HEMA) = 1.75.

Degassed dimethylformamide solutions containing the polymer Fast Red A, and L-ascorbic acid in Pyrex tubes were irradiated for 3-5 min in a merry-go-round apparatus thermostatted at 20° C. Light of $\lambda = 313$ nm was isolated with a potassium chromate filter solution. A Riko Kagaku 400-W medium-pressure mercury lamp was used. Dimethylformamide was purified by azeotropic distillation with benzene and water, followed by fractional distillation. The concentrations of the ingredients were so adjusted that ca. 95% of the incident light was absorbed by the anthraquinone unit ($\epsilon_{313\text{nm}} = 4300$ liter/mole-cm) and ca. 5% by Fast Red A ($\epsilon_{313\text{nm}} = 5000$ liter/mole-cm). The reduction of Fast Red A by direct absorption was found to be negligible under the irradiation conditions used. The initial decrease in Fast Red A absorption at 520 nm was monitored to measure the extent of oxidation-reduction between L-ascorbic acid and Fast Red A. The rate of formation of O-alkylated anthrahydroquinone derivatives (Table 2) was determined on the following basis: no significant decrease (less than 2%) in anthraquinone absorption at 400 nm occurs during the initial stage of irradiation; the decrease in Fast Red A absorption at 400 nm is proportional to that at 520 nm; the reduced form of Fast Red A does not absorb light at 400 nm, and finally the extinction coefficient of the anthrahydroquinone derivatives at 400 nm is 5900 liter/mole-cm [9].

RESULTS AND DISCUSSION

When irradiated, the dimethylformamide solutions of the copolymers, Fast Red A (FRA), and L-ascorbic acid (AsA) underwent spectral changes as indicated in Fig. 1; the absorption due to FRA, $\lambda_{max} = 520$ nm, decreased, while new absorption bands around 400 nm emerged and rose gradually. These bands have been assigned to 9,10-anthrahydroquinone and its O-alkylated derivatives [9]. Our previous study with a monomer model compound, [2-(9,10-anthraquinonyl)]-methyl acetate, did not show such absorption bands of comparable magnitude until amost all FRA had been consumed. This observation is thus unique in polymeric systems.

Since no direct reduction of FRA occurs in the absence of the monomeric or polymeric sensitizer under the irradiation conditions

TABLE 1. Copolymerization of AQMMA with HEMA[a]

Polymer	Monomer feed (mole %)		Polymer composition		Mean sequence length[b]		$[\eta]$ (dl/g)[c]
	AQMMA	HEMA	f_{AQMMA}	f_{HEMA}	$\bar{\ell}_{AQMMA}$	$\bar{\ell}_{HEMA}$	
Polymer 10	20.3	79.7	0.10	0.90	1.01	7.87	–
Polymer 23	39.5	60.5	0.23	0.77	1.03	3.78	0.44
Polymer 29	49.0	51.0	0.29	0.71	1.05	2.82	0.23
Polymer 43	67.5	32.5	0.43	0.57	1.10	1.84	0.32
Polymer 53	87.7	12.3	0.53	0.47	1.36	1.26	–

[a] Conditions: 1.3×10^{-3} mole monomers in 1 ml of dimethylformamide at 60°C for 1-2 hr with 0.5 wt % of azobisisobutyronitrile. Abbreviations: AQMMA, [2-(9,10-anthraquinonyl)]methyl methacrylate; HEMA, 2-hydroxyethyl methacrylate.

[b] Calculated from estimated monomer reactivity ratios, r_1 (AQMMA) = 0.05 and r_1 (HEMA) = 1.75, and initial monomer concentrations.

[c] Measured in dimethylformamide at 30°C.

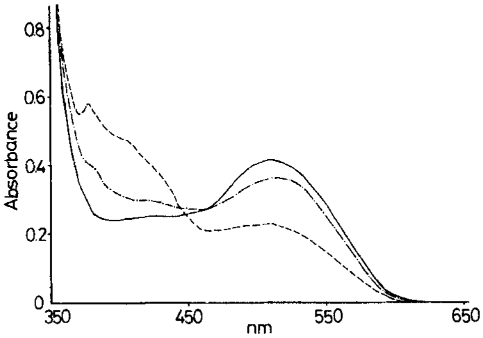


FIG. 1. Spectral change of dimethylformamide solution containing Polymer 53 (AQMMA 53 mole %; HEMA 47 mole %), Fast Red A, and L-ascorbic acid: (—) 0 min; (- · -) 3 min; (- -) 10 min. Conditions: [AQ] = 5.0×10^{-4} mole/liter, [FRA] = 3.3×10^{-5} mole/liter, [AsA] = 2.0×10^{-2} mole/liter. Irradiated at 313 nm and 20° C.

employed and the naphthalene unit quenches the anthraquinone triplet (^{3}AQ*) and thus lowers the quantum yield of photosensitization, the photochemical scheme shown in Eqs. (1)-(6) was proposed for the sensitized oxidation-reduction of AsA and FRA [8].

Energy absorption:

$$^1\mathrm{AQ} + h\nu \xrightarrow{I_a} {}^1\mathrm{AQ}^*(\pi - \pi^*) \tag{1}$$

Intersystem crossing:

$$^1\mathrm{AQ}^* \xrightarrow{k_i} {}^3\mathrm{AQ}^*(n - \pi^*) \tag{2}$$

Internal conversion:

$$^3\mathrm{AQ}^* \xrightarrow{k_d} {}^1\mathrm{AQ} \tag{3}$$

Photoreduction:

$$^3\mathrm{AQ}^* + \mathrm{AsA} \xrightarrow{k_1} \mathrm{AQH_2} + \mathrm{AsA(-H_2)} \tag{4}$$

Thermal reduction:

$$\mathrm{AQH_2} + \mathrm{FRA} \xrightarrow{k_r} {}^1\mathrm{AQ} + \mathrm{FRAH_2} \tag{5}$$

Photoadduct formation:

$$^3AQ^* + HEMA \xrightarrow{k_2} AQ\text{-}HEMA \qquad (6)$$

Intersystem crossing of $^1AQ^*$ to $^3AQ^*$ is known to proceed with a quantum yield of nearly unity [10]. The possibility of FRA reduction via triplet FRA formed by energy transfer from $^3AQ^*$ was excluded, because the presence of copolymerized naphthalene unit ($E_T = 60.9$ kcal/mole), which efficiently quenches $^3AQ^*$ ($E_T = 62.7$ kcal/mole), does not increase but decrease the quantum yield of FRA reduction, even though triplet naphthalene formed has a triplet energy far above that of FRA($E_T < 45$ kcal/mole) and a far longer triplet life time ($\tau_T \sim 2$ sec) than that of $^3AQ^*$ ($\tau_T \sim 10^{-2}$ sec) and thus is expected to transfer its energy to FRA more efficiently than $^3AQ^*$ [10, 11]. The concentration of FRA, 3.3×10^{-5} mole/liter, seems to be too low to effect energy transfer from $^3AQ^*$ or from triplet naphthalene to FRA. A small amount of triplet FRA formed by direct excitation or by energy transfer seems to deactivate without reacting with AsA present in the system at a concentration of 2×10^{-2} mole/liter. 9,10-Anthraquinone, on the other hand, has an infinite lifetime and thus is capable of reducing FRA . (The polarographic halfwave potentials of 9,10-anthraquinone and 1,1'-azonaphthalene, a parent molecule of FRA, are $E_{1/2}$ (SEC)= -0.51 and -0.335 V, respectively [12].

When irradiated samples were allowed to stand in the dark for several days, no further spectral changes were observed which indicates that the absorption around 400 nm is not due to AQH_2, but due to its unreactive and stable O-alkylated derivatives (photoadducts). The relative quantum yields of FRA reduction and photoadduct formation are listed in Table 2. It should be noted that the higher the content of HEMA, the lower the relative quantum yield of FRA reduction. The quantum yield of photoadduct formation, on the other hand, increases with increasing HEMA content, indicating that the HEMA units in the polymer are involved in photoadduct formation. The ethylene hydrogens in the side chain of the HEMA residues are likely to be abstracted by $^3AQ^*$, followed by combination of the resulting two radicals to give O-alkylated derivatives of AQH_2 [Eq. (6)].

Thus, Eq. (7) is obtained for the ratio of the quantum yield of the two photochemical reactions,

$$\phi_{ad}/\phi_{-FRA} = k_2[HEMA]/k_1[AsA] \qquad (7)$$

where [HEMA] is the local concentration of the HEMA unit in the vicinity of the excited AQ unit, not the overall HEMA concentration with respect to the solution. Since polymer solutions used are all

TABLE 2. Rate and Relative Quantum Yield of Photochemical Reactions[a]

Polymer	FRA reduction		Adduct formation	
	Rate × 10^{-6} (mole/liter-min)	Relative quantum yield ϕ_{-FRA}	Rate × 10^{-6} (mole/liter-min)	Relative quantum yield ϕ_{ad}
Polymer 23	1.21	1	9.0	2.11
Polymer 29	1.34	1.19	7.14	1.67
Polymer 43	1.85	1.53	4.98	1.17
Polymer 53	2.26	1.87	4.26	1

[a] Conditions: [AQ] = 5.0×10^{-4} mole/liter, [FRA] = 3.3×10^{-5} mole/liter, [AsA] = 2.0×10^{-2} mole/liter, irradiated at 313 nm in dimethylformamide at 20° C. Abbreviations: FRA, Fast Red A; AsA, L-ascorbic acid; AQ, anthraquinone unit.

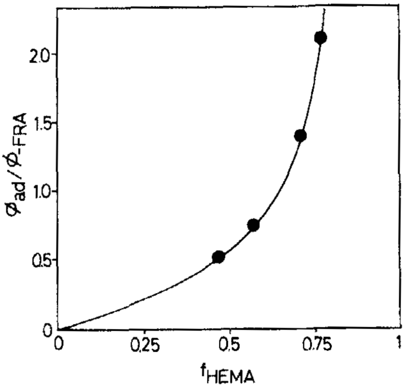


FIG. 2. Plot of quantum yield ratio against HEMA mole fraction in polymer.

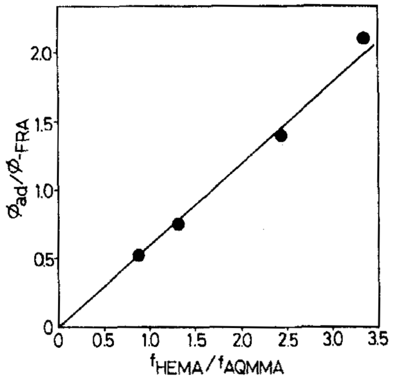


FIG. 3. Plot of quantum yield ratio against ratio of HEMA to AQMMA mole fraction in polymer.

dilute, i. e., [AQ] = 5.0×10^{-4} mole/liter, only the HEMA units in the same polymer chain as the excited AQ unit must be involved. This assumption is supported by the fact that no appreciable decrease in solubility due to intermolecular crosslinking was observed. The mole fraction of HEMA in the polymer, f_{HEMA}, may thus be a suitable parameter for the local HEMA concentration. Plotting the quantum yield ratio against f_{HEMA}, however, gave an upward curve (Fig. 2). When f_{HEMA}/f_{AQMMA} was used instead of f_{HEMA} (Fig. 3), a good linear relationship was obtained. This seems to suggest that not only the AQ unit initially excited but other AQ units in the vicinity are involved in the reaction with AsA and thus in the subsequent reduction of FRA. Two well known interactions between excited and near-by ground state chromophores are energy migration and excimer formation [1-5]; the extreme case of the former is an energy delocalization leading to an increased efficiency of photoreaction, while the latter gives an adverse effect, i. e., concentration effect or self-quenching of the excited state [7]. What we generally observe is the sum of these two effects. When excitation energy is assumed to be delocalized among the AQ units in the AQMMA sequence where the initial excitation occurs, the rate of AQH_2 formation will be proportional to the mean sequence length of AQMMA ($\bar{\ell}_{AQMMA}$), i. e., $k_1' \bar{\ell}_{AQMMA}[AsA]$. The rate of adduct formation, on the other hand, will be $k_2' \bar{\ell}_{AQMMA} f_{HEMA}/f_{AQMMA}$, since the number of HEMA units per an AQMMA sequence is $100f_{HEMA}$ divided by $100f_{AQMMA}/\bar{\ell}_{AQMMA}$, or $\bar{\ell}_{AQMMA} f_{HEMA}/f_{AQMMA}$. Equation (7) will thus become:

$$\frac{\phi_{ad}}{\phi_{-FRA}} = \frac{k_2' f_{HEMA}}{k_1'[AsA] f_{AQMMA}} \tag{8}$$

The linear relationship for a fixed concentration of AsA in Fig. 3 supports the preceding discussion. The question is then: how extensive is the energy delocalization? Even though it cannot be excluded that the migration range extends over several AQMMA sequences owing to a coiled conformation of the polymer, the reasonable range seems to be a single AQMMA sequence where AQ units are nearest neighbors to one another along the polymer chain. Energy migration or more generally energy transfer involving triplet energy is known to occur within a distance comparable to the collisional distance of the chromophores [13], and methacrylate polymers are known to be well solvated in moderately hydrogen-bonding solvents of solubility parameters around 24×10^3 J/m^3, to which dimethylformamide belongs [14]; AQ units in different AQMMA sequences are not likely to be involved in energy delocalization. We may then interpret f_{HEMA}/f_{AQMMA} as $\bar{\ell}_{HEMA}/\bar{\ell}_{AQMMA}$, the ratio of the mean lengths of the two monomer sequences, since

$$\bar{\ell}_{AQMMA} = (r_1[AQMMA]_0/r_2[HEMA]_0) + 1$$

$$\ell_{HEMA} = (r_2[HEMA]_0/r_1[AQMMA]_0) + 1$$

and

$$f_{AQMMA} = \bar{\ell}_{AQMMA}/(\bar{\ell}_{AQMMA} + \bar{\ell}_{HEMA})$$

$$f_{HEMA} = \bar{\ell}_{HEMA}/(\bar{\ell}_{AQMMA} + \bar{\ell}_{HEMA})$$

Thus,

$$f_{HEMA}/f_{AQMMA} = \ell_{HEMA}/\ell_{AQMMA}$$

Generally, the values of ℓ_{HEMA}/ℓ_{AQMMA} are slightly larger than those of f_{HEMA}/f_{AQMMA}, which is reasonable, since even at a low conversion of polymerization (< 10%) the actual mean sequence of the more reactive monomer tends to be slightly shorter than that calculated, while that of the less reactive one slightly longer than that calculated. Nevertheless, a fairly good linear relationship is obtained when the ratios of the mean sequence lengths, instead of those of the mole fractions, are plotted against the quantum yield ratios. Thus, even though most of the AQ units are isolated as seen in Table 1, the small fraction of the AQMMA sequences with two or more AQ units will have triplet energy delocalization, and the HEMA sequences nearest to the AQMMA sequence are likely to be involved in chemical quenching of the AQ triplet state and thus in the formation of AQ-HEMA photoadduct.

REFERENCES

[1] T. Ishii, T. Handa, and S. Matsunaga, Macromolecules, 11, 40 (1978).

[2] M. T. Vala, Jr., J. Haebig, and S. A. Rice, J. Chem. Phys., 43, 886 (1965).

[3] R. B. Fox, T. R. Price, R. F. Cozzens, and J. R. McDonald, J. Chem. Phys., 57, 534 (1972).

[4] C. David, M. Lempereur, and G. Geuskens, Eur. Polym. J., 8, 417 (1972).

[5] A. C. Somersall and J. B. Guillet, Macromolecules, 6, 218 (1973).

[6] K. Kojima, S. Iwabuchi, T. Nakahira, T. Uchiyama, and Y. Koshiyama, J. Polym. Sci. Polym. Letters Ed., 14, 143 (1976).

[7] T. Nakahira, C. Minami, S. Iwabuchi, and K. Kojima, Makromol. Chem., 179, 1593 (1978).

[8] T. Nakahira, E. Shinomiya, T. Fukumoto, S. Iwabuchi, and K. Kojima, Eur. Polym. J., 14, 317 (1978).

[9] A. Ledwith, G. Ndaalio, and A. R. Taylor, Macromolecules, 8, 1 (1975).
[10] S. A. Carlson and D. M. Hercules, J. Am. Chem. Soc., 93, 5611 (1971).
[11] S. L. Murov, Handbook of Photochemistry, Marcel Dekker, New York, 1973.
[12] S. Koide, in: Constants of Organic Compounds, M. Kotani, Ed., Asakura, Tokyo, 1963.
[13] A. A. Lamola, in: Energy Transfer and Organic Photochemistry, A. A. Lamola and N. J. Turro, Eds., Wiley-Interscience, New York, 1969.
[14] H. Burrell, in: Polymer Handbook, J. Brandrup and E. H. Immergut, Eds., Wiley, New York, 1970.

Accepted by editor May 17, 1979
Received for publication June 14, 1979