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Magnetic Field Effects on the Intramolecular Photoreaction of *n*-Alkyl Anthraquinone-2-carboxylates

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In the photoreaction of *n*-alkyl anthraquinone-2-carboxylates, AQ-*n*, magnetic field effects were observed in the decay of biradicals, the formation rate and the yield of cage products and the disappearance yield of AQ-*n*. The results are interpreted in terms of the radical pair mechanism. Chain length dependence of the disappearance yield indicates that singlet-triplet energy degeneracy of biradicals occurs when $n>10$.

Studies of magnetic field effects (MFE) on photochemical reactions continue to be of fundamental interest because of their central role in spin dynamics of radical reactions. After the first observation of MFE on the photolysis of dibenzoyl peroxide in 1976,[1] we have studied a number of photochemical reactions of aromatic ketones.[2] Especially, we have deeply concerned with MFE on their photoreactions in aqueous micellar solution. It is because radical pairs generated in a micellar cage exhibit remarkable effects. In the previous papers,[3,4] we reported MFE on the end-to-end photoreaction of bifunctional chain molecules as a model reaction between aromatic molecules solubilized in a micellar cage. Although surfactant molecules composing micellar cages act also as a hydrogen donor in quite a few photoreactions reported,[2] no MFE study on intramolecular photoreaction modeling this type of reaction was reported. In order to elucidate the mechanism of MFE and the role of a micellar cage, we designed intramolecular photoreactions of anthraquinone and benzophenone derivatives having a long methylene side chain as a model reaction of the respective ketone and surfactant molecules in a micellar cage. In laser flash photolysis, however, no appreciable MFE was observed on the photoreaction of *n*-alkyl benzophenone-4-carboxylates, most probably due to the slow intramolecular hydrogen abstraction rate in the excited triplet states.

In this paper,[5] we describe MFE on the intramolecular hydrogen abstraction of *n*-alkyl anthraquinone-2-carboxylates (AQ-*n*), studied with the aid of laser flash photolysis, two-step laser-induced fluorescence and steady-state photolysis. In this system, we can see considerable MFE on product yield and others, though the overall reaction rate is mainly controlled by the hydrogen abstraction in the excited triplet states. Chain length dependence of MFE on the disappearance yield of AQ-*n* indicates that singlet-triplet energy degeneracy of the biradicals occurs with $n>10$.

Experimental

Chemicals. *n*-Alkyl anthraquinone-2-carboxylates (AQ-*n*) were available from the previous work.[6] EP grade 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) was purified by a column of basic aluminum oxide (1 m). This solvent was used in order to minimize the hydrogen abstraction from the solvent. Sample solutions (10^{-4} M) were deaerated by repeated freeze-pump-thaw cycles, when necessary (1 M=1 mol dm^{-3}).

Apparatus. Transient absorption spectra were obtained by using an XeCl excimer laser (308 nm) and a xenon arc lamp as an exciting and a probe light source, respectively. Transient signal on a storagescope was fed into a microcomputer for analysis.

Two-step laser-induced fluorescence (TS-LIF) was measured by using an excimer laser (308 nm) and an N_2 laser-pumped dye laser (430 nm) as the first and the second laser. A homemade variable delay circuit was used for the timing of two lasers.

In steady-state photolysis, a 3 ml aliquot of the aerated sample solution was irradiated with a 500 W xenon arc lamp filtered with a combination of filters (λ_{max}=330 nm). Relative yield ϕ of disappearance of AQ-*n* was determined from the initial UV spectral change around 320 nm.

Magnetic fields were applied with a conventional electromagnet. Details of the apparatus were described elsewhere.[6]

Results and Discussion

Reaction Mechanism. In a previous paper,[6] we studied photoinduced intramolecular hydrogen abstraction reaction of *n*-alkyl anthraquinone-2-carboxylates AQ-*n* (n=2—20), by steady-state photolysis, phosphorescence, laser flash photolysis, and TS-LIF measurements. Photophysics and photochemistry of AQ-*n* in deaerated Freon 113 solution are described by the following scheme:

$$\text{AQ-}n \longrightarrow {}^1\text{AQ*-}n \qquad (1)$$

$$ {}^1\text{AQ*-}n \longrightarrow {}^3\text{AQ*-}n \qquad (2)$$

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$$^{3}\mathrm{AQ}^{*}\text{-}n \longrightarrow \mathrm{AQ}\text{-}n + \mathrm{phos.} \tag{3}$$

$$^{3}\mathrm{AQ}^{*}\text{-}n \longrightarrow \mathrm{AQ}\text{-}n \tag{4}$$

$$^{3}\mathrm{AQ}^{*}\text{-}n \longrightarrow {}^{3}\mathrm{BR}\text{-}n \tag{5}$$

$$^{3}\mathrm{BR}\text{-}n \longrightarrow {}^{1}\mathrm{BR}\text{-}n \tag{6}$$

$$^{1}\mathrm{BR}\text{-}n \longrightarrow \mathrm{P}\text{-}n \tag{7}$$

The excited triplet ^{3}AQ*-*n* of the anthraquinone moiety is generated by photoexcitation ((1) and (2)). While it phosphoresces (3), it abstracts a hydrogen atom from its methylene side chain, affording to a triplet biradical, ^{3}BR-*n*, composed of an anthrasemiquinone and an alkyl radical (5). Triplet (T)-singlet (S) intersystem crossing (ISC) (6) is followed by the recombination of two radical centers to form cyclic cage products, P-*n* (7). Reactive methylene cites, from which a hydrogen atom is abstracted and at which cage recombination takes place, may be distributed among the chain in proportion to the collision probability of the aromatic moiety and the chain.

Remarkable *n* dependence of the relative yield of disappearance of AQ-*n*, the lifetime and yield of ^{3}AQ*-*n* (phosphorescence and laser flash photolysis) and yield of P-*n* (laser flash photolysis and TS-LIF) were observed. These results are attributable to the reaction (5), which is controlled by the collision probability between the methylene chain and the excited triplet anthraquinone moiety. In order to see how distances of two radical centers affect MFE on present biradicals, photoreaction of AQ-*n* were examined.

Laser Flash Photolysis. In the laser flash photolysis of the deaerated Freon 113 solution of AQ-*n*, an intense absorption band appears around 380 nm. In general, the transient spectra within the 100 μs time scale might be composed of at least three species, i.e., ^{3}AQ*-*n*, BR-*n*, and P-*n*. Decay curves of AQ-*n* exhibit non-exponential decay as reported in a previous paper.[6] The decay component (decaytime, 50 (*n*=2)—4 μs (*n*=20)) is mainly attributable to the absorption of ^{3}AQ*-*n*, as they are comparable with the phosphorescence lifetimes (76 (*n*=2)—4 μs (*n*=20)). Spectral assignment of BR-*n* is rather difficult, as their absorption may be covered by those of ^{3}AQ*-*n*. The decaytimes of ^{3}BR-*n* at zero field seem to be controlled by the lifetime of ^{3}AQ*-*n*, as the risetimes of P-*n* are compatible with the phosphorescence lifetimes.[6] Absorption intensities left at the late stage of the decay may be attributable to photoproducts P-*n*, since the spectra are similar to those of photoproducts observed in the steady-state photolysis and risetimes of P-*n* monitored by TS-LIF is comparable to the lifetimes of ^{3}AQ*-*n*.

Small but appreciable MFE were observed for the decay curves of long-chain molecules with *n*=18 and 20 (Fig. 1 and Table 1), though AQ-*n* with *n*<18 exhibited no appreciable effect. In the case of AQ-20, the apparent decaytime monitored at 380 nm increases from 4.5 μs at zero field to 5.9 μs in the presence of a magnetic field (1 T). The decay component exhibiting MFE is definitely assigned to the absorption of BR-*n* (*n*=18, 20), though it may be hidden by the intense absorption of ^{3}AQ*-*n* at zero field.

Table 1. Magnetic Field Effects on the Decaytime (τ_{LP}) of Transient Absorption Monitored at 380 nm and the Risetime (τ_{R}) of TS-LIF Intensity Monitored at 520 nm[a)]

	τ_{LP}/μs		τ_{R}/μs	
	0 T	1 T	0 T	1 T
AQ-18	4.9	6.8	—	—
AQ-20	4.5	5.9	4.9	6.3

a) Experimental errors are ±15%.

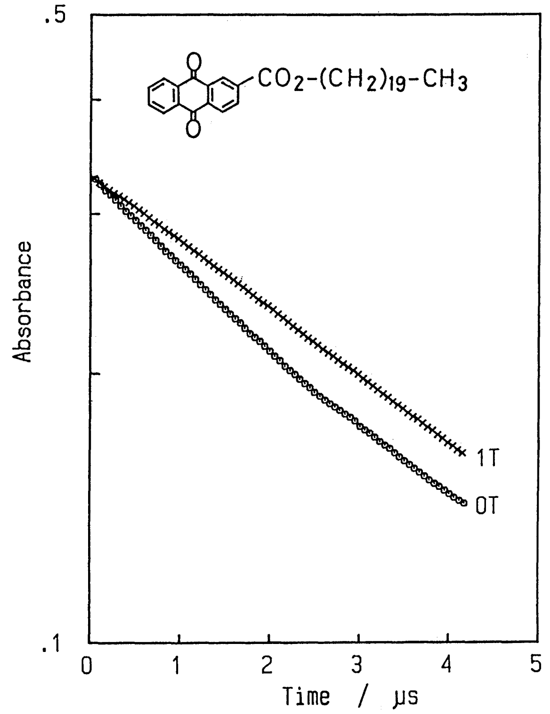

Fig. 1. (a) Magnetic field effects on the decay of transient absorption of AQ-20 monitored at 380 nm in deaerated Freon 113 solution.

The results imply that T-S ISC of ^{3}BR-18 and ^{3}BR-20 occurs via electron-nuclear hyperfine (hf) interaction at zero field and that the rate is reduced in a magnetic field, because of the Zeeman splitting of triplet sublevels, as observed for the photoreaction of anthraquinones in micellar solution.[7] No MFE on the transient absorption of AQ-*n* with *n*<18 may be attributable to the slow decay rate of ^{3}AQ*-*n* as described above.

Because of local high concentration of surfactant, hydrogen abstraction of excited triplet anthraquinone from a surfactant molecule in a micellar cage is very fast (<10 ns).[7] Thus in micellar solution we can see significant MFE on the radical pair composed of the semiquinone and a radical derived from the surfactant by laser flash photolysis. In the present model system, however, small effects are observed only for long chain molecules because hydrogen abstraction is more than hundred times slower in the present intramolecular reaction than in the bimolecular reaction in micellar solution.

Two-Step Laser-Induced Fluorescence (TS-LIF). In steady-state photolysis, intense fluorescence of photoproducts, P-n, generated from the recombination reaction (7) appears around 500 nm. Thus, MFE on the yield of P-n were examined by TS-LIF technique. In the present experimental setup, TS-LIF was detected for P-n with n>8, where an efficient intramolecular reaction took place in ^{3}AQ*-n. Agreement of risetimes of P-n (17.5 (n=10)—4.7 μs (n=20)) with the lifetimes of ^{3}AQ*-n mentioned in the above section, indicates that reaction in ^{3}AQ*-n is the rate-determining step.

Figure 2 shows MFE on the time profile of TS-LIF of P-20 monitored at 520 nm. Risetime of P-20 increases slightly in the presence of a magnetic field (1 T) with the concomitant decrease in intensity (Table 1). The change in the risetime is in good agreement with that in the decaytime of ^{3}BR-20 mentioned above.

Table 2. Magnetic Field Effects on the TS-LIF Intensity at 20 μs Delay after Laser Excitation Monitored at 520 nm

AQ-n	$Q^{a)}$/%
AQ-10	−32±10
AQ-12	−27
AQ-14	−28
AQ-16	−24
AQ-18	−29
AQ-20	−24

a) Q is the TS-LIF intensity change induced by the presence of a magnetic field (1 T).

Table 2 shows MFE on the yield change of P-n obtained from the TS-LIF intensities at 20 μs delay after the first laser excitation. Obviously the yields decrease by about 20—30% in a magnetic field. The results indicate that rate of product formation (P-2O) and yield of cage products, P-n (n=10—20), decrease due to the reduction of T-S ISC rate in a magnetic field as expected. In this reaction, bimolecular reactions (8) and (9), competing with T-S ISC in ^{3}BR-n, may be responsible to the reduction of P-n yield, though they are not shown in the above scheme.

$$ {}^3\mathrm{BR}\text{-}n + \text{impurity (or solvent)} \longrightarrow \qquad (8) $$

$$ {}^3\mathrm{BR}\text{-}n + {}^3\mathrm{BR}\text{-}n \longrightarrow \qquad (9) $$

Steady-State Photolysis. Steady-state photolysis was carried out in aerated Freon 113 solution. In aerated solution, oxidation of the anthrasemiquinone moiety, which competes with T-S ISC, may regenerate the anthraquinone one as observed in the photoreaction of anthraquinone in micellar solution.[8]

$$ {}^3\mathrm{BR}\text{-}n + \mathrm{O_2} \rightarrow \rightarrow \mathrm{AQ}\text{-}n \text{ (or } \mathrm{AQ'}\text{-}n) \qquad (10) $$

Oxidation of the corresponding alkyl radical center may result in the regeneration of original alkyl chain (AQ-n) or the generation of an unsaturated chain (AQ′-n), though its fate is unclear in the UV spectral measurements. Thus the yield of disappearance of AQ-n is expected to be affected by a magnetic field.

Figure 3 shows MFE on the relative yield ϕ of disappearance of AQ-14 in aerated Freon 113 solution. The reduction of T-S ISC rate in ^{3}BR-14 caused by a magnetic field leads to an increase in the yield of a competing reaction process (10). A remarkable decrease in the yield occurs at low field (<0.05 T). In the presence of oxygen, the lifetime of ^{3}BR-14 may be determined by the reaction with oxygen in higher

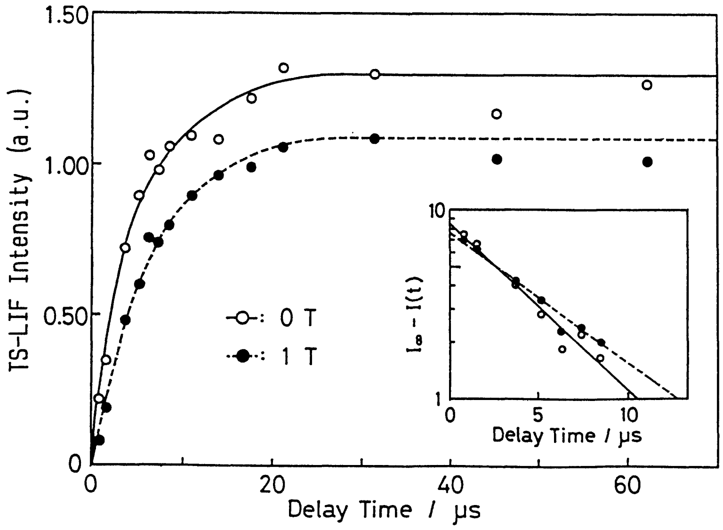

Fig. 2. Magnetic field effects on the rise of TS-LIF of AQ-20 monitored at 520 nm in deaerated Freon 113 solution. Inest: Semi-logarithmic plots of the intensities $I(t)$. Here, the intensity at 31 μs delay is used as I_∞.

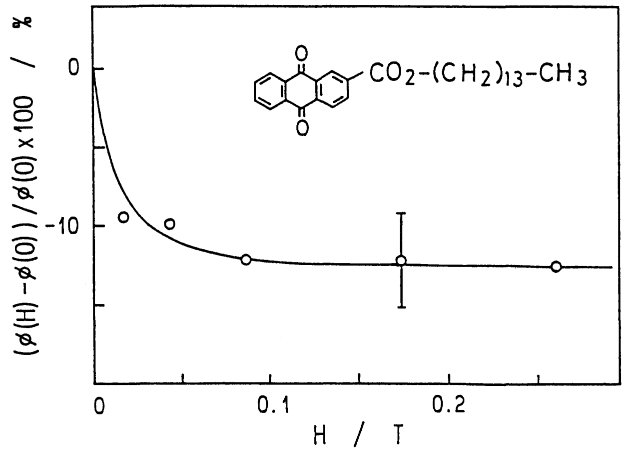

Fig. 3. Magnetic field dependence of the relative yield $\phi(H)$ of disappearance of AQ-14 in aerated Freon 113 solution. A typical experimental error is given by an error bar.

magnetic field, and, for this reason, saturation of MFE occurs at low field.

Next, influence of chain length on ϕ was examined (Fig. 4). In the presence of a magnetic field (0.26 T), ϕ decreases by about 10% for long chain molecules with $n>10$, whereas no effect is observed for short chain molecules. Sharp change of the effects is observed between $n=10$ and 12. The chain length dependence of MFE was revealed by steady-state photolysis measurements, though we failed to examine it by transient measurements as mentioned above.

An S-T energy gap of a biradical arises from the electron exchange interaction and decreases exponentially with increasing interradical distance. When a chain length is long ($n>10$), T-S ISC of biradicals occurs via hf interaction at zero field in the chain conformations in which the energy gap is comparable to the hf energy. In the presence of a high magnetic field, the ISC rate is reduced due to the Zeeman splitting of triplet sublevels. When the distance is short ($n<12$), the exchange interaction determining the S-T energy gap becomes much larger than the hf interaction and T-S ISC caused by hf interaction becomes of minor importance. Under the circumstances, the Zeeman splitting of triplet sublevels in a magnetic field does not affect appreciably the ISC rate of biradicals. In other words, Fig. 4 implies that S-T energy degeneracy of BR-n occurs when $n>10$.

Chain-linked biradicals may be divided into two groups, i.e., biradicals exhibiting sharp chain length dependence of MFE and those exhibiting gradual dependence. Singlet ionic biradicals generated from phenanthrene-$(CH_2)_n$-dimethylaniline,[9] pyrene-$(CH_2)_n$-dimethylaniline,[10] and neutral triplet ones generated from cyclic ketones[11] belong to the former group. In the case of phenanthrene-$(CH_2)_n$-dimethylaniline, for example, drastic change of MFE on exciplex fluorescence intensity is observed between $n=8$ and 10. On the other hand, triplet biradicals generated from xanthone-COO-$(CH_2)_n$-OCO-xanthene[3] and benzophenone-O-$(CH_2)_n$-O-diphenylamine[4] are classified in the second group. In these cases, considerable MFE are observed even for the short chain biradicals in which the S and T states are likely non-degenerate, and magnitude of the effects increases gradually with increasing the chain length. The difference between two groups seems attributable to the magnetic-field-independent deactivation rate from the respective biradical states. When the lifetime of a biradical is short, ISC occurs only between degenerate states and its MFE is sharply affected by the chain length. In the case of biradicals in which no fast magnetic-field-independent process is involved, ISC may also take place between slightly non-

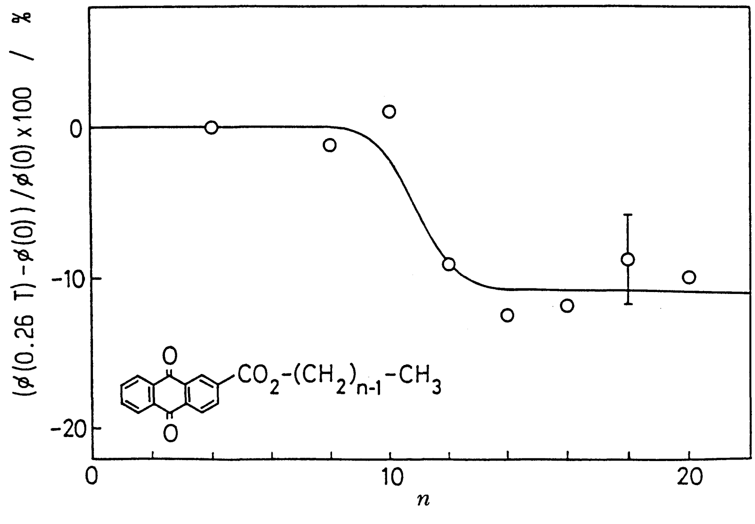

Fig. 4. Chain length dependence of the relative yield ϕ of disappearance of AQ-n in the presence and absence of a magnetic field (0.26 T) in aerated Freon 113 solution. A typical experimental error is given by an error bar.

degenerate states, and, for this reason, change of MFE upon chain length is not sharp. Chain length dependence of disappearance of AQ-*n* shown in Fig. 4 may be comparable with those of biradicals composed of well-defined radical centers mentioned above, and ^{3}BR-*n* may be classified into the first group. It is because location of alkyl radical center is considered to mostly localize at the penultimate methylene carbon for $n<16$, taking into account of the fact that, in the reaction of *n*-alkyl benzophenone-4-carboxylates (BP-*n*, $n=14$—20), the reactive methylene site is considerably localized (50—70%) at the penultimate methylene when the chain becomes short ($n=14$ and 16).[12)] In the present biradicals, the fast reaction with oxygen, estimated to be about 5×10^6 sec^{-1}, may be responsible for shortening of biradical lifetimes.

According to the conformational calculation of BP-*n*,[13)] distances from the methylene carbon atom adjacent to the ester group to the methyl carbon atom are about 0.89 nm (BP-10) and 1.04 nm (BP-12). Thus, the distance between two radical centers (presumably the carbon atom at hydroxyl group and the penultimate carbon atom at the alkyl chain) of BR-12 is estimated to be longer than 1 nm. Thus, we may make rough estimation that the distance between two unpaired electrons in the biradicals must be long (>1 nm) for appearance of MFE. From the present model study, the interradical distance of a radical pair composed of anthrasemiquinone and a surfactant-derived radical generated in a micellar cage is estimated to be >1 nm. Furthermore, agreement of the present results with those of our previous MFE studies on the bifunctional chain molecules[3,4,9,14)] and those reported by other groups[10,11)] leads to a general conclusion that S-T degeneracy of biradicals occurs at the interradical distance of 1 nm or so.

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References

1) Y. Tanimoto, H. Hayashi, S. Nagakura, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **41**, 267 (1976).

2) Y. Tanimoto and M. Itoh, In "Physical Organic Chemistry 1986," ed by M. Kobayashi, Elsevier, Amsterdam (1987), p. 257; Y. Tanimoto, *Yakugaku Zasshi*, **109**, 505 (1989).

3) Y. Tanimoto, M. Takashima, K. Hasegawa, and M. Itoh, *Chem. Phys. Lett.*, **137**, 330 (1987); Y. Tanimoto, M. Takashima, and M. Itoh, *Bull. Chem. Soc. Jpn.*, **62**, 3923 (1989).

4) Y. Tanimoto, N. Okada, S. Takamatsu, and M. Itoh, *Bull. Chem. Soc. Jpn.*, **63**, 1342 (1990).

5) Y. Tanimoto, M. Takashima, M. Uehara, M. Itoh, M. Hiramatsu, R. Nakagaki, T. Watanabe, and S. Nagakura, *Chem. Lett.*, **1985**, 15.

6) Y. Tanimoto, M. Uehara, M. Takashima, and M. Itoh, *Bull. Chem. Soc. Jpn.*, **61**, 3121 (1988).

7) Y. Tanimoto, H. Udagawa, and M. Itoh, *J. Phys. Chem.*, **87**, 724 (1983).

8) Y. Tanimoto, K. Shimizu, and M. Itoh, *J. Am. Chem. Soc.*, **106**, 7257 (1984).

9) Y. Tanimoto, N. Okada, M. Itoh, K. Iwai, K. Sugioka, F. Takemura, R. Nakagaki, and S. Nagakura, *Chem. Phys. Lett.*, **136**, 42 (1987); Y. Tanimoto, K. Hasegawa, N. Okada, M. Itoh, K. Iwai, K. Sugioka, F. Takemura, R. Nakagaki, and S. Nagakura, *J. Phys. Chem.*, **93**, 3586 (1989).

10) A. Weller, H. Staerk, and R. Treichel, *Faraday Discuss. Chem. Soc.*, **78**, 271 (1984): H. Staerk, W. Kuhnle, R. Treichel, and A. Weller, *Chem. Phys. Lett.*, **118**, 19 (1985).

11) M. B. Zimmt, C. Doubleday, Jr., and N. J. Turro, *J. Am. Chem. Soc.*, **107**, 6726 (1985).

12) R. Breslow and M. A. Winnik, *J. Am. Chem. Soc.*, **91**, 3083 (1969).

13) D. S. Saunders and M. A. Winnik, *Macromolecules*, **11**, 18 (1978).

14) R. Nakagaki, M. Hiramatsu, K. Mutai, Y. Tanimoto, and S. Nagakura, *Chem. Phys. Lett.*, **134**, 171 (1987).