CHEMISTRY LETTERS, pp. 631-634, 1994.

Enormously Long Triplet Lifetime of Zinc(II) Tetraphenylporphyrin Incorporated As a Pendant of a Liquid Crystalline Polymethacrylate Based on Cholesterol Mesogens

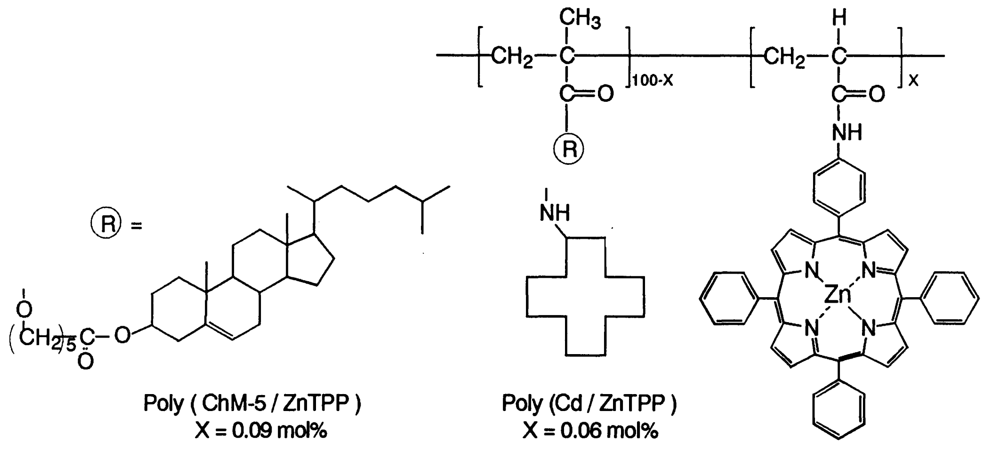
Yotaro MORISHIMA,* Shin-ichi YUSA, Kazunori SAEGUSA, Kohji TASHIRO, and Mikiharu KAMACHI*
Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560

A small number of zinc(II) tetraphenylporphyrin (ZnTPP) moieties were covalently incorporated into a liquid crystalline (LC) polymethacrylate bearing cholesterol side chains. The ZnTPP moieties exhibited enormously long triplet lifetime in the LC polymethacrylate in *n*-hexane.

We have reported that amphiphilic copolymers of sodium 2-acrylamido-2-methylpropanesulfonate (AMPS) with hydrophobic comonomers carrying such bulky side-chains as lauryl, cyclododecyl, and 1-adamantyl groups adopt unimolecular (unimer) micelles comprised of hydrophobic clusters of the side-chains in aqueous solution.1-5) In contrast to the dynamic nature of conventional surfactant micelles, the unimer micelles are "static" with all charged and hydrophobic groups covalently linked to the polymer backbone.

Recently, we have recognized that zinc(II) tetraphenylporphyrin (ZnTPP) moieties covalently compartmentalized in the hydrophobic cluster of such unimer micelles show unusual photophysical and photochemical behavior.6) Of particular interest was that phosphorescence and E-type delayed fluorescence (thermal repopulation from the triplet-excited state (T_1)) were emitted by the compartmentalized ZnTPP moieties in aqueous solution at room temperature.6) These unusual observations are primarily due to the fact that T-T annihilation is prevented because the ZnTPP groups are "statically" isolated from each other in the hydrophobic cluster such that the ZnTPP triplets have virtually no chance to encounter each other during their lifetimes. This, in turn, leads to long triplet lifetime even in fluid aqueous solution at room temperature.6) These findings suggest that rigorous isolation of ZnTPP chromophores in any organized molecular assemblies of static nature may bring about the same effect. These considerations prompted us to incorporate the ZnTPP moieties into a mesophase of a liquid-crystalline (LC) side-chain polymer.

In this study, we prepared a copolymer of cholesteryl 6-methacryloyloxyhexanate (ChM-5) and a small mole fraction of zinc(II) 5-(4-acrylamidophenyl)-10,15,20-triphenylporphynate (ZnAATPP). The mesogenic methacrylate monomer ChM-5 was prepared according to the literature7) with some modifications, and ZnAATPP was synthesized as previously.2) The copolymerization of ChM-5 (99.9 mol%) and ZnAATPP (0.1 mol%) was performed in the presence of 2,2'-azobis(2-methylpropionitrile) (AIBN) (0.5 mol% on the basis of the total monomers) in tetrahydrofuran (THF) at 60 °C for 24 h in a vacuum-sealed ampule. The copolymer (61.6% conversion) was purified by reprecipitating from THF into a large excess of acetone three times. The content of the ZnAATPP unit in the copolymer was determined by UV-visible absorption spectroscopy to be 0.09 mol% by assuming the molar extinction coefficient at the Soret band of the ZnAATPP unit in the copolymer to be the same as that of ZnAATPP6) ($\varepsilon = 6.42 \times 10^5$ M^{-1}cm^{-1}). Weight average molecular weight of the copolymer was estimated to be 5.4x10^4 (M_w/M_n=1.7) by GPC with polystyrene standards. As a reference, the copolymer of 0.06 mol% ZnAATPP with *N*-cyclododecylmethacrylamide1) (CdMAm) (M_w=1.1x10^5, M_w/M_n=2.3 by GPC) was also prepared in a manner similar to the preparation of the copolymer of ZnAATPP and ChM-5. In the text, the copolymers of ZnAATPP with ChM-5 and with CdMAm are abbreviated as poly(ChM-5/ZnTPP) and poly(Cd/ZnTPP), respectively (Scheme I).



Scheme 1.

Laser photolysis was performed by using a rhodamine 590 dye laser (Quanta-Ray PDL-3) pumped by the second harmonics of a Q-switched Nd:YAG laser (Quanta-Ray DCR-2). The output energy of the dye laser was adjusted to ca. 12 mJ/pulse at 560 nm, a wavelength at which sample solutions were excited. To avoid the effect of a trace of oxygen, the sample solutions were completely outgassed by several pump-and-thaw cycles on a high vacuum line.

The copolymer poly(ChM-5/ZnTPP) was soluble in nonpolar hydrocarbons such as *n*-hexane, cyclohexane, benzene, and toluene. An interesting observation to be noted was that a concentrated *n*-hexane solution (ca. 10 wt%) of poly(ChM-5/ZnTPP) exhibited birefringence under a polarizing microscope. An x-ray diffraction pattern of the *n*-hexane solution of poly(ChM-5/ZnTPP) recorded with a MAC Science DIP100 X-ray diffraction system (Cu Kα) is shown in Fig. 1. A broad diffraction pattern with a peak at ca. 20° in 2θ was observed. These observations imply that poly(ChM-5/ZnTPP) forms an LC phase in the concentrated *n*-hexane solution, although the detailed structure of the lyotropic mesophase has yet to be determined.

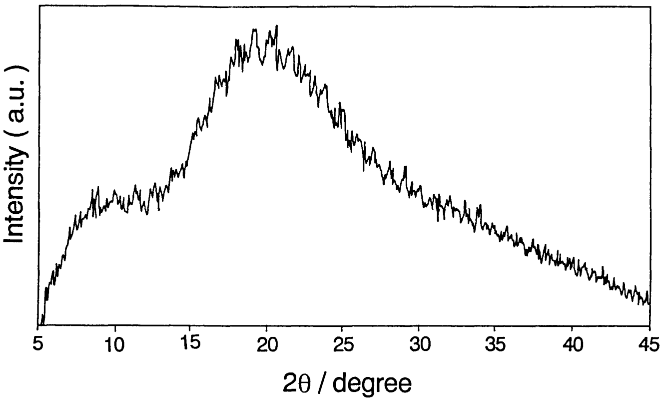


Fig. 1. X-ray diffraction pattern of poly(ChM-5/ZnTPP) in concentrated *n*-hexane solution.

Figure 2 shows time-resolved transient absorption spectra of poly(ChM-5/ZnTPP) in *n*-hexane at room temperature. The spectra were assigned to the T-T absorption spectra of the ZnTPP moiety by comparing with the reference spectra of ZnTPP itself.8) Importantly, the T-T absorption bands of poly(ChM-5/ZnTPP) persisted for a surprisingly long time. In Fig. 3, are compared the decays of the T-T absorption for poly(ChM-5/ZnTPP) in *n*-hexane and in benzene. The triplet decay in *n*-hexane was found to be much slower than that in benzene. The decay in *n*-hexane followed first-order kinetics with a triplet lifetime (τ_T) of 18 ms, while there was a significant fraction of a faster decay component in benzene. This implies that the ZnTPP moieties are more rigorously isolated from each other in a microenvironment of poly(ChM-5/ZnTPP) in *n*-hexane than they are in benzene. Since the concentration of the *n*-hexane solution in this experiment was very low, the existence of the mesophase was not recognized. However, the extremely long triplet lifetime observed for the *n*-hexane solution of poly(ChM-5/ZnTPP) suggests that even in a dilute *n*-hexane solution, the ZnTPP moieties exist in an intramolecular assembly of the pendant cholesterol mesogens probably with LC order, whereby T-T annihilation of the ZnTPP triplets are thoroughly prevented.

In the reference copolymer, a small mole fraction of ZnTPP pendants are inserted in the array of bulky cyclododecyl pendants. This situation may also bring about a suppression of the T-T annihilation due to steric protection of the ZnTPP groups by the neighboring bulky cyclododecyl pendants. Fig. 4 compares the decays of the T-T absorption for the benzene solutions of poly(ChM-5/ZnTPP), poly(Cd/ZnTPP), and small molecular weight ZnTPP. Benzene was used as solvent because poly(Cd/ZnTPP) was not soluble in *n*-hexane. As can be seen from Fig. 4, in the time region of ca. 3 ms, the triplet decays of poly(ChM-5/ZnTPP) and poly(Cd/ZnTPP) apparently followed first-order kinetics. The apparent triplet lifetime of poly(ChM-5/ZnTPP) (τ_T=4.9 ms) was found to be significantly longer than that of poly(Cd/ZnTPP) (τ_T=1.8 ms). In the case of small molecular weight ZnTPP, on the

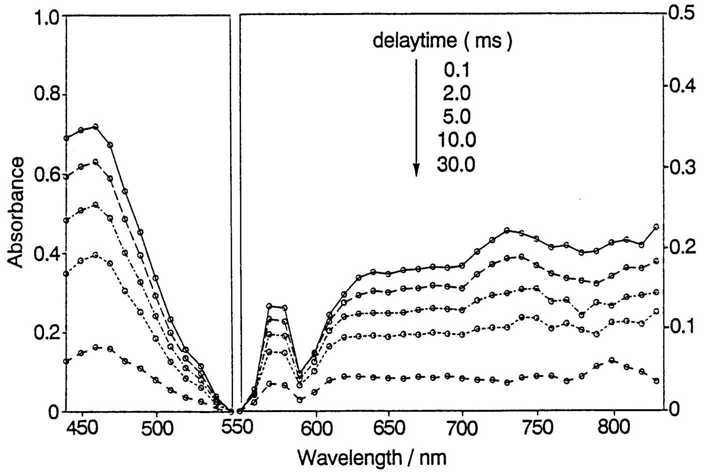


Fig. 2. Time-resolved transient absorption spectra for poly(ChM-5/ZnTPP) in *n*-hexane at room temperature; [ZnTPP](residue)=15 μ*M*. Delay times are indicated in the figure.

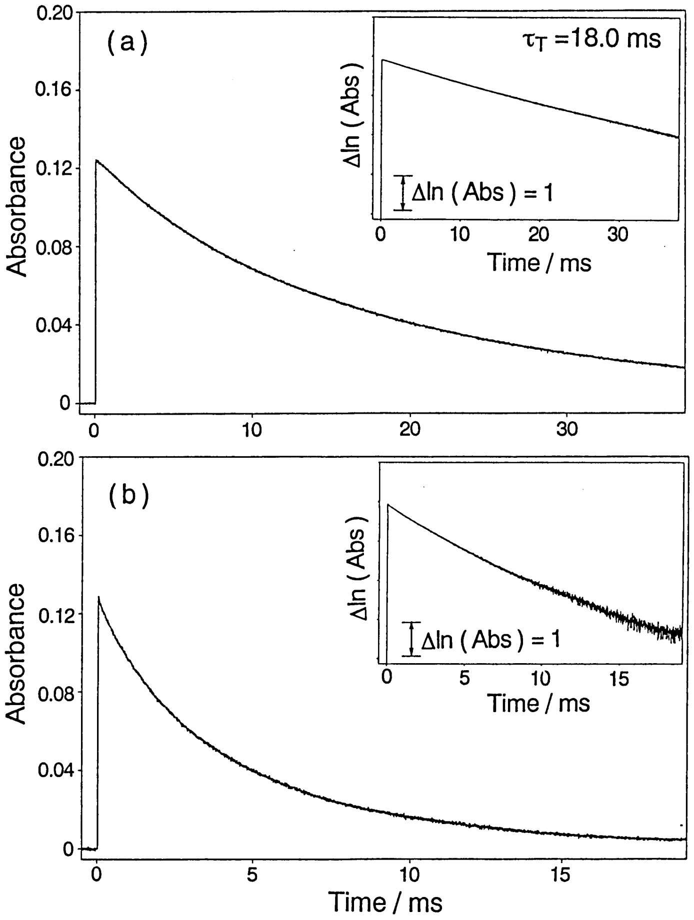


Fig. 3. Comparison of decay profiles for the T-T absorption monitored at 480 nm for poly(ChM-5/ZnTPP); (a) in *n*-hexane, (b) in benzene; [ZnTPP](residue)=15 μ*M*; at room temperature. Inserts: first-order plots of the decay data.

other hand, the triplet decay followed second-order kinetics, indicating that T-T annihilation is the predominant path for triplet deactivation under the conditions of this experiment ([ZnTPP]=15 μ*M*; laser power, 12 mJ/pulse).

In summary, the ZnTPP moieties in poly(ChM-5/ZnTPP) exhibited enormously long triplet lifetime in *n*-hexane arising presumably from the isolation of the chromophores in an intramolecularly organized assembly of the mesogenic cholesterol pendants with LC order, which prevents the ZnTPP groups from encountering each other, and thereby T-T annihilation is rigorously prevented. In the reference copolymer, although each ZnTPP pendant exists in the crowd of bulky cyclododecyl pendants, the ZnTPP triplets are likely to encounter with each other due to dynamic motions of the polymer chain during the lifetime of the triplets, and thus T-T annihilation was not completely prohibited.

This work was supported in part by the Grant-in-Aid for Scientific Research (B) from the Ministry of Education, Science and Culture, Japan.

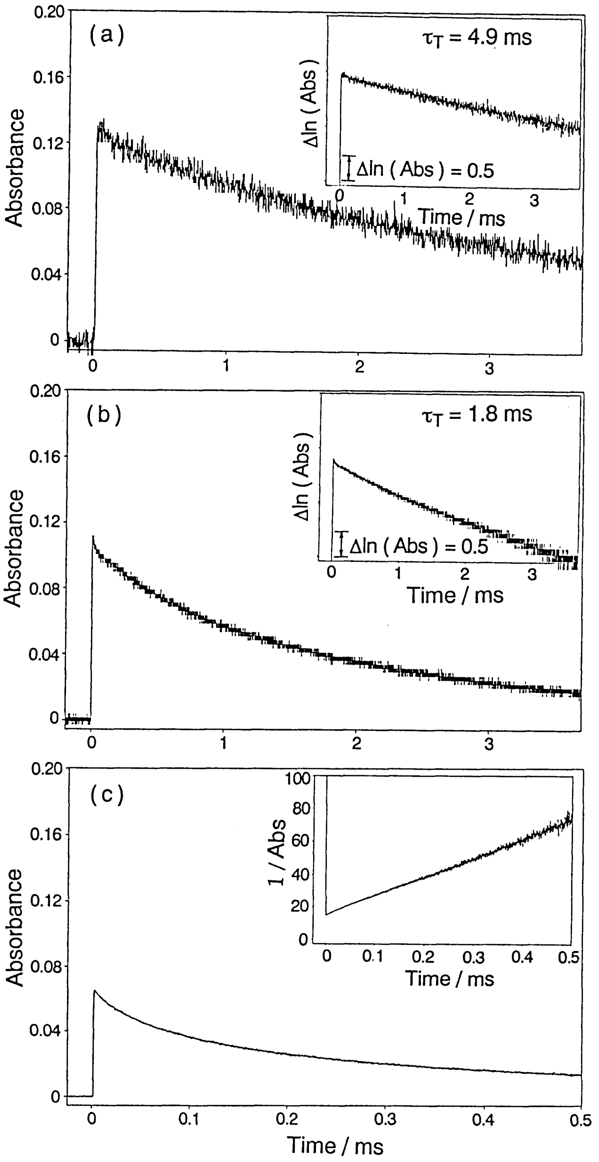


Fig. 4. Comparison of decay profiles for the T-T absorption in benzene monitored at 480 nm; (a) poly(ChM-5/ZnTPP), (b) poly(Cd/ZnTPP), (c) ZnTPP; [ZnTPP](residue)=15 μ*M*, at room temperature. Inserts: first-order (or second-order) plots of the decay data.

References

1) Y. Morishima, Y. Tominaga, M. Kamachi, T. Okada, Y. Hirata, and N. Mataga, *J. Phys. Chem.*, **95**, 6027 (1991).
2) Y. Morishima, M. Tsuji, M. Kamachi, and K. Hatada, *Macromolecules*, **25**, 4406 (1990).
3) Y. Morishima, M. Seki, Y. Tominaga, and M. Kamachi, *J. Polym. Sci., Polym. Chem. Ed.*, **30**, 2099 (1991).
4) M. Seki, Y. Morishima, and M. Kamachi, *Macromolecules*, **25**, 6540 (1992).
5) Y. Morishima, M. Tsuji, M. Seki, and M. Kamachi, *Macromolecules*, **26**, 3299 (1993).
6) H. Aota, Y. Morishima, and M. Kamachi, *Photochem. Photobiol.*, **57**, 989 (1993).
7) P. J. Shannon, *Macromolecules*, **16**, 1677 (1983).
8) A. Harriman, G. Porter, and N. Searle, *J. Chem. Soc., Faraday Trans. 2*, **75**, 1515 (1979).

(Received December 20, 1993)