JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 24
1988

Molecular Weight Control of Photopolymerization at an Oriented Bilayer Surface using Phase Separation of Fluorocarbon- and Hydrocarbon-amphiphiles

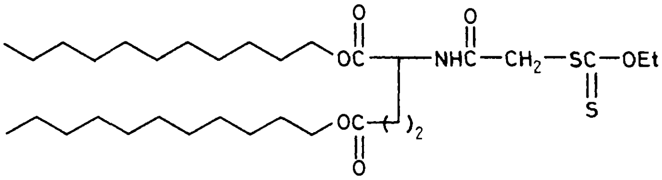
Nobuyuki Higashi, Takato Adachi, and Masazo Niwa*

Department of Applied Chemistry, Faculty of Engineering, Doshisha University, Kamikyo-ku, Kyoto 602, Japan

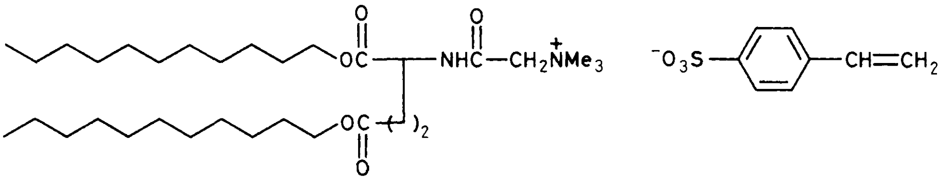
Binary bilayer membranes composed of a polymerizable hydrocarbon amphiphile and a non-polymerizable fluorocarbon amphiphile form a phase-separated bilayer, and the molecular weight of the polymer produced upon photoinitiation can be controlled by the phase separation of the bilayer.

Much attention has been paid to the polymerization of bilayer membranes because of the practical and biological interest that polymerized vesicles should show enhanced stabilities.[1] We have reported that ultrahigh molecular weight polymers in a bilayer state can be produced under mild conditions by taking advantage of the well-defined bilayer surface and fixation of the photoinitiator at an effective position.[2]

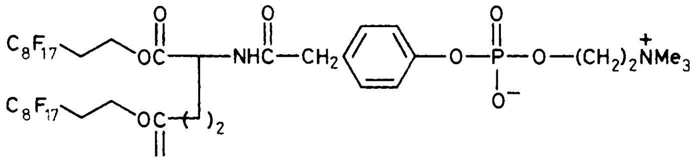
We report that the molecular weight of polymers formed at a bilayer surface can be controlled using the phase separation of the binary bilayer mixture composed of the polymerizable hydrocarbon amphiphile (**2**) and the non-polymerizable fluorocarbon amphiphile (**3**). Fluorocarbons are not readily miscible with hydrocarbons. This property has been used to control the phase separation of the bilayer membrane of double-chain fluorocarbon amphiphiles from the corresponding hydrocarbon bilayer.[3,4] No report has appeared, however, on molecular weight-control of the polymer formed at a membrane surface by phase-separated bilayers.



(1)



(2)



(3)

We employed (**1**)[2] and (**2**)[2] as photoinitiator and polymerizable amphiphile, respectively. Clear solutions were obtained when ternary mixtures of the newly prepared zwitterionic fluorocarbon amphiphile (**3**),† (**1**), and (**2**) ($[\mathbf{1}] + [\mathbf{2}] + [\mathbf{3}] = 60$ mM, $[\mathbf{1}] = 0.6$ mM, $[\mathbf{3}]/\{[\mathbf{2}] + [\mathbf{3}]\} = 0 - 0.5$) were dispersed in water by sonication. Differential scanning calorimetry (d.s.c.) of the single-component bilayer of (**2**) gave an endothermic peak at 35.2 °C due to the gel-to-liquid crystal phase transition.[2] When small amounts of (**1**) ($[\mathbf{1}]/[\mathbf{2}] = 1/100$, molar ratio) were added into (**2**), the peak temperature (35.0 °C) in d.s.c. was close to that of (**2**), which might indicate that the incorporation of (**1**) into (**2**) bilayer matrix did not affect the physical state of the membrane. In the case of the ternary mixture ($[\mathbf{3}]/\{[\mathbf{2}] + [\mathbf{3}]\} = 0.4$), an endothermic peak in the d.s.c. thermogram, which was slightly broader than that of the (**2**) bilayer, was observed at 35.0 °C, consistent with the phase transition temperature of the (**2**) bilayer. This result implies that the two bilayers [(**2**) and (**3**)] are almost completely immiscible and form a domain over each other. The phase separation is caused by the poor miscibility of the hydrocarbon component with the fluorocarbonic membrane phase.

We prepared five types of aqueous bilayer solutions with different compositions ($[\mathbf{3}]/\{[\mathbf{2}] + [\mathbf{3}]\} = 0, 0.1, 0.2, 0.4$, and 0.5). Photopolymerizations were carried out using u.v. irradiation with a low-pressure mercury lamp at 30 °C in a Pyrex tube under N_2 atmosphere after degassing. Aqueous dispersions became slightly turbid after irradiation but no precipitate was observed.

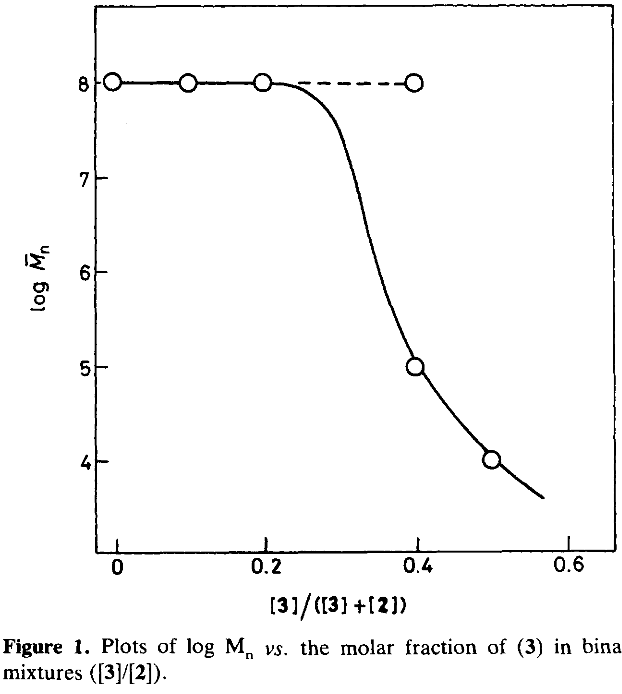
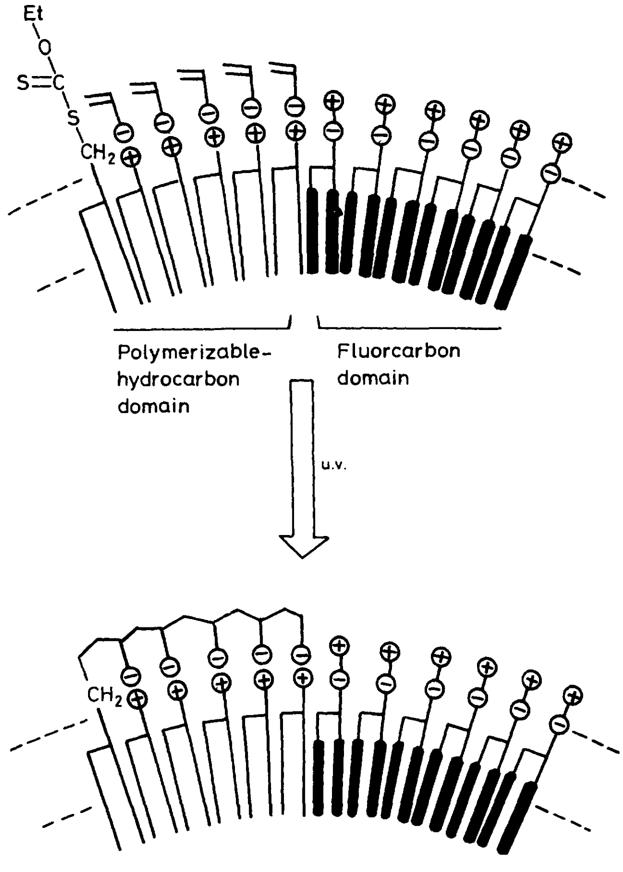


Figure 1. Plots of log M_n *vs.* the molar fraction of (**3**) in binary mixtures ($[\mathbf{3}]/[\mathbf{2}]$).

The photopolymerization process of these aqueous solutions can be monitored by absorption spectroscopy. The absorption maximum at 256 nm, which corresponds to the styrene sulphonate moiety of (**2**), decreased rapidly upon irradiation and a new peak due to the formation of polymer appeared at 225 nm. After 4 h of irradiation the monomer peak disappeared almost completely. Similar trends were observed for the other four samples. These spectral data may suggest that photopolymerizations proceed effectively in the phase-separated polymerizable hydrocarbon aggregates containing small amounts of photoinitiator, consistent with the results of d.s.c. as described above.

Gel permeation chromatographic (g.p.c.) measurements for each polymerized sample were carried out as described before.[2] In Figure 1, log $\bar{M}_n$, calculated from the polystyrene standard on the basis of g.p.c. curves, is plotted against the fraction of fluorocarbon amphiphiles ($[\mathbf{3}]/\{[\mathbf{2}] + [\mathbf{3}]\}$) in the mixed bilayer membranes. When the fraction of fluorocarbon is below 0.2, the molecular weight of the polymers reaches $\sim 10.^{8}$ This implies that the domain size of fluorocarbon-components in the bilayer matrices may be too small to affect the molecular weight of polymers formed. When the fraction increases to 0.4, two kinds of polymer are generated: *i.e.*, high molecular weight (10^8) and low molecular weight (10^5) polymers. We do not have any direct evidence for explaining this phenomenon, but it could be postulated that the formation of high and low molecular weight polymers is due to an inter-vesicular polymerization and an intravesicular polymerization, respectively. The fact that the aggregation morphology of amphiphile (**2**) drastically changes from a well developed vesicle to a tube-like aggregate upon photopolymerization, which will be described elsewhere, supports such a



Scheme 1

---

† The new compound (**3**) was prepared as follows. L-Glutamic acid-bis-(1*H*,1*H*,2*H*,2*H*-perfluorodecyl) ester was prepared according to the literature.[3] The diester was treated with *p*-hydroxyphenyl acetate in the presence of diethyl cyanophosphate as a condensing agent, and then treated with 2-chloro-2-oxo-1,3,2-dioxaphospholane.[5] The final product was obtained from the reaction of this phospholane derivative with excess of trimethylamine, yield 30%, R_f 0.9 (chloroform–methanol). The structure was confirmed by n.m.r. spectroscopy and elemental analyses.

postulate. Above 0.5 (the fraction of fluorocarbon), an extremely low molecular weight polymer ($\overline{M}_n = 10^4$) with 100% conversion is formed. This is probably due to preferential photopolymerization in the phase-separated, polymerizable hydrocarbon domain.

In conclusion, a binary bilayer membrane composed of polymerizable hydrocarbon amphiphile and non-polymerizable fluorocarbon amphiphile can control the molecular weight of polymer produced with an effective photoinitiation, by using the phase separation of the bilayer as shown in Scheme 1. Precise control of the molecular weight would require morphological studies of the bilayer membranes.

We thank Dainippon Ink and Chemicals, Inc., Tokyo for the gift of perfluoro alcohol.

Received, 27th June 1988; Com. 8/02546K

References

1 H. Bader, K. Dorn, K. Hashimoto, B. Hupfer, J. H. Petropoulos, H. Ringsdorf, and H. Sumitomo, 'Polymeric Membranes,' Ed. M. Godon, Springer–Verlag, Berlin, 1985, p. 1; J. A. Hayward, D. S. Johnson, and D. Chapman, *Ann. N.Y. Acad. Sci.*, 1985, **446**, 267; D. F. O'Brien, R. T. Klingbiel, D. P. Specht, and P. N. Tyminski, *ibid.*, 1985, **446**, 282; S. L. Regen, *ibid.*, 1985, **446**, 296; J. H. Fendler, *ibid.*, 1985, **446**, 308.

2 N. Higashi, T. Adachi, and M. Niwa, *Macromolecules*, 1988, **21**, 1190.

3 T. Kunitake, S. Tawaki, and N. Nakashima, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 3235; T. Kunitake and N. Higashi, *J. Am. Chem. Soc.*, 1985, **107**, 692; T. Kunitake and N. Higashi, *Makromol. Chem. Suppl.*, 1985, **14**, 81.

4 R. Buschl, T. Folda, and H. Ringsdorf, *Makromol. Chem. Suppl.*, 1984, **6**, 245.

5 R. S. Edmondson, *Chem. Ind.* (*London*), 1962, 1828.