all suffer from disadvantages. The direct synthesis[9] of **3** from glycerol and ethylene carbonate requires repeated distillations. Conversion[10] of 3-*O*-benzylglycerol to **3** exposes the carbonate to AcOH over a long period of time while the benzyl group is hydrogenolyzed and also uses an expensive starting material. When the (allyloxy)carbonyl group[11] is present on the precursor to **3**, its removal leaves **3** in an aqueous solution. Other approaches to **3** involve multistep sequences[12] or employ highly toxic glycidyl derivatives.[13] The present synthesis of **3** uses inexpensive starting materials and volatile solvents and results in minimal glycerol formation.

The only previous synthesis of **4** was via transesterification of **3** with methyl methacrylate followed by distillation.[7b] An advantage of the acid chloride condensation is that heating is not required and the time during which solvent- and inhibitor-free **4** must be handled is minimized. The polymerization of neat **4** to a glass occurs in a few hours at room temperature under vacuum.

A major obstacle to the preparation of tractable **1** is the high probability of cross-linking reactions. These can occur at two sites, either at di- or trimethacryloylglycerol units (due to monomer impurities) or at the tertiary 2-carbon of the glyceride. Prevention of cross-linking can be accomplished by polymerizing to low conversion or by careful monomer purification, both of which call for the sacrifice of a considerable amount of monomer. Other changes in polymerization conditions might also be effective.

In summary, a convenient synthesis of **4** has been devised and the polymerization of **4** has been examined. Soluble **1** has been obtained for the first time, although further experiments will be necessary in order to optimize the yield of tractable **1**.

Experimental Section

4-(Hydroxymethyl)-1,3-dioxolan-2-one (3). A solution of **2** (40 g) in 500 mL of MeOH was blanketed with N_2. The N_2 current was diminished, and 10% Pd on carbon (6 g) was added. (**DANGER**: The dry catalyst may ignite on prolonged contact with MeOH vapor and oxygen!) Toluenesulfonic acid hydrate (4 g) was added and the mixture was stirred at ambient temperature. Aliquots of 1 mL were periodically removed, filtered through Al_2O_3, concentrated, and assayed by NMR. After 8 h, deallylation was >95% complete. The mixture was filtered through 250 mL of neutral Al_2O_3 wet with MeOH, and the Al_2O_3 was rinsed with 700 mL of additional MeOH. The combined filtrates were concentrated at reduced pressure and the residue distilled at 130 °C and 0.2 torr on a kugelrohr (higher distillation temperatures can cause glycidol formation). Yield, 20.3 g of **3** (68%); ^{1}H NMR (Me_2SO-d_6) δ 3.6 (m, 2 H), 4.2–4.7 (m, 2 H), 4.9 (m, 1 H), 5.3 (t, 1 H, J = 10 Hz, OH); ^{13}C NMR (Me_2SO-d_6) δ 60.6, 65.8, 77.0, 155.1 (CO). (**CAUTION**: The Pd/C/Al_2O_3 residue should not be allowed to dry but instead should be promptly suspended in H_2O for disposal. Otherwise, the residue may smolder or ignite.

(2-Oxo-1,3-dioxolan-4-yl)methyl 2-Methyl-2-propenoate (4). A mixture of freshly distilled **3** (6.4 g, 0.057 mol), THF (90 mL), and NEt_3 (dried with KOH and distilled from P_2O_5, 8.0 mL, 0.05 mol) was mechanically stirred at 0 °C under Ar. Methacryloyl chloride (90%, 6.4 mL, 0.052 mol) dissolved in THF (30 mL) was added dropwise with stirring over 50 min, keeping the temperature below 5 °C. After 10 min of further stirring, the solution was filtered and the solids were extracted with 100 mL of Et_2O. The combined filtrates were washed with concentrated aqueous NaCl, first at pH 2 and then at pH 8, dried, filtered, and concentrated to 7.7 g of crude **4** (77%). Purification by flash chromatography on Al_2O_3, eluting with Et_2O, gave 3.5 g of **4** (35%): ^{1}H NMR ($CDCl_3$) δ 2.0 (m, 3 H, CH_3), 4.2–4.7 (m, 4 H), 5.0 (m, 1 H), 5.6 (m, 1 H), 6.1 (m, 1 H).

Poly[(2-oxo-1,3-dioxolan-4-yl)methyl 2-methyl-2-propenoate] (1). Monomer **4** (2.1 g) was dissolved in 80 mL of toluene and the solution was purged with Ar. Azobis(isobutyronitrile) (20 mg) was added, and the solution was stirred 43 h at 60–65 °C. The mixture was poured into 450 mL of MeOH and the polymer thus precipitated was collected, washed with MeOH, and dried under vacuum. The yield was 1.24 g of **1** as a white powder, soluble in DMF and Me_2SO, insoluble in less polar solvents (THF, CH_3CN) and H_2O: T_g 120 °C; ^{1}H NMR (Me_2SO-d_6) δ 0.6–2.1 (5 H), 3.8–5.3 (5 H), all very br; ^{13}C NMR (Me_2SO-d_6) δ 17 (CH_3), 44 (quaternary C), 53 (br, CH_2 in backbone), 65 (br), 66, 74, 155 (carbonate CO), 177 (ester CO); IR (KBr pellet) 2960, 1805 (carbonate CO), 1734 (ester CO), 1170. Anal. Calcd for $(C_8H_{10}O_5)_n$: C, 51.60; H, 5.41. Found: C, 51.30; H, 5.48. Molecular weight 30 000 ● 10 000 (intrinsic viscosity in DMF).

Acknowledgment. We are most grateful to M. L. Kaplan for the synthesis and donation of an initial sample of **2** and to M. Y. Hellman for the molecular weight determination. We also thank G. N. Taylor, E. Reichmanis, and A. Shugard for helpful discussions.

Registry No. 1, 109013-85-6; 2, 826-29-9; 3, 931-40-8; 4, 13818-44-5; $H_2C{=}C(Me)COCl$, 920-46-7.

References and Notes

(1) Tasaka, S.; Miyasato, K.; Yoshikawa, M.; Miyata, S.; Ko, M. *Ferroelectrics* **1984**, *57*, 267–276.
(2) Kaplan, M. L.; Rietman, E. A.; Cava, R. J.; Holt, L. K.; Chandross, E. A., unpublished results, Xia, D. W.; Smid, J. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 617–621.
(3) Hardy, L. C.; Shriver, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 3823–3828.
(4) Singer, K. D.; Lalama, S. J.; Sohn, J. E.; Small, R. D. *SPIE Abstracts*, San Diego, 1986.
(5) Williams, D. J., Ed. *Nonlinear Optical Properties of Organic and Polymeric Materials*; American Chemical Society, Washington, DC, 1983; ACS Symp. Ser. No. 233.
(6) For example, ethylene carbonate has μ = 4.87 D. Riddick, J. A.; Bunder, W. B. *Organic Solvents*; Wiley: New York, 1970.
(7) (a) Fang, J. C., U.S. Patent 2 967 173 1961. (b) Obrien, J. L.; Beavers, E. M. U.S. Patent 2 979 514, 1961.
(8) For example: Schneider, K.; Naarmann, H. European Patent Appl. 1088, 1979.
(9) Bell, J. B., Jr.; Currier, V. A.; Malkemus, J. D. U.S. Patent 2 915 529, 1959.
(10) Cunningham, J.; Gigg, R. *J. Chem. Soc.* **1965**, 1553–1554.
(11) Guibe, F.; Saint M'Leux, Y. *Tetrahedron Lett.* **1981**, *22*, 3591–3594.
(12) Zhelvakova, E. G.; Magnashevskii, V. A.; Ermakova, L. I.; Shvets, V. I.; Preobrazhenskii, N. A. *Zh. Org. Khim.* **1970**, *6*, 1987–1992.
(13) Rokicki, G., Kuran W. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1662–1666.

Approach to the χ Function for Ternary Solutions Containing Two Polymers in a Pure Solvent

YOSHIYUKI EINAGA,* ZHEN TONG, and
HIROSHI FUJITA

Department of Macromolecular Science, Osaka University, Toyonaka, Osaka 560, Japan. *Received December 2, 1986*

We consider a ternary solution consisting of a pure solvent (component 0) and two monodisperse polymers (components 1 and 2) in which the partial molar volume of each component is independent of composition and pressure p. The total volume V of the solution is represented by

$$V = V_0(n_0 + P_1n_1 + P_2n_2) \qquad (1)$$

where n_i and P_i are the amount in moles and the relative chain length of component i, the latter being defined by

$$P_i = V_i/V_0 \qquad (2)$$

with V_i the molar volume of component i. The volume

0024-9297/87/2220-2027$01.50/0

fraction ϕ_i of component i is given by

$$\phi_i = V_i n_i / V = P_i n_i / (n_0 + P_1 n_1 + P_2 n_2) \qquad (3)$$

Since $\phi_0 + \phi_1 + \phi_2 = 1$, the composition of the solution is specified by the set of variables (ϕ_1, ϕ_2). We note that it may also be specified by the set of variables (ϕ, ξ_1), where ϕ is the overall volume fraction of the mixture of polymers 1 and 2, i.e.,

$$\phi = \phi_1 + \phi_2 \qquad (4)$$

and ξ_1 $(=1 - \xi_2)$ is the volume fraction of polymer 1 in this mixture, i.e.,

$$\xi_1 = \phi_1 / (\phi_1 + \phi_2) \qquad (5)$$

If the Flory–Huggins athermal solution formed by these three components is chosen as a reference system, the chemical potential μ_0 of the solvent in our ternary solution is expressed by

$$\mu_0 = \mu_0^0 + RT\,[\ln(1 - \phi) + (1 - P_n^{-1})\phi + \chi(\phi_1, \phi_2, T, p)\phi^2] \qquad (6)$$

Here, μ_0^0 is the value of μ_0 in the pure state, R the gas constant, T the absolute temperature, P_n the number-average relative chain length of the polymer mixture defined by

$$P_n^{-1} = \xi_1 P_1^{-1} + \xi_2 P_2^{-1} \qquad (7)$$

and χ a function of composition, T, and p which lumps both enthalpic and entropic deviations of μ_0 in our ternary system from that in the reference system. Any means enabling us to determine the chemical potential difference $\mu_0 - \mu_0^0$ can be used to evaluate χ.

This paper aims to show that χ can be expressed as follows:

$$\chi = \xi_1^2 \chi_{11}^{b}(\phi_1) + \xi_2^2 \chi_{22}^{b}(\phi_2) + 2\xi_1\xi_2\chi_{12}^{t}(\phi_1, \phi_2) \qquad (8)$$

Here, $\chi_{ii}^{b}(\phi_i)$ $(i = 1, 2)$ is the χ function for the binary solution of solvent 0 and polymer i in which the polymer volume fraction is ϕ_i and $\chi_{12}^{t}(\phi_1, \phi_2)$ the contribution to χ from all types of interaction between the molecules of polymers 1 and 2 in the ternary solution considered. Though not explicitly shown, all terms in eq 8 refer to fixed T and p.

Derivation of Equation 8

Subject to the assumption that the partial molar volume of the solvent is independent of composition and pressure, the osmotic pressure π^* of our ternary solution at fixed T and μ_0 is given by

$$V_0 \pi^* = -\mu_0(\phi_1, \phi_2, T, p) + \mu_0^0(T, p) \qquad (9)$$

Following Kurata,[1] π^*/RT can be expanded in powers of mass concentration C_1 and C_2 as

$$\pi^*/RT = \sum_{i=1}^{2} C_i/M_i + (1/2)\sum_{i=1}^{2}\sum_{j=1}^{2} B_{ij} C_i C_j + (1/3)\sum_{i=1}^{2}\sum_{j=1}^{2}\sum_{k=1}^{2} B_{ijk} C_i C_j C_k + \ldots \qquad (10)$$

where M_i is the molecular weight of polymer i and B_{ij}, B_{ijk}, etc., which are functions of T and μ_0, are invariant with exchange of subscripts. Subject to the assumption that the partial specific volumes of polymers 1 and 2 are independent of composition, eq 10 can be rewritten

$$V_0 \pi^*/RT = P_n^{-1}\phi + (1/2)\sum_{i=1}^{2}\sum_{j=1}^{2} D_{ij}\phi_i\phi_j + (1/3)\sum_{i=1}^{2}\sum_{j=1}^{2}\sum_{k=1}^{2} D_{ijk}\phi_i\phi_j\phi_k + \ldots \qquad (11)$$

where

$$D_{ij} = V_0 B_{ij}/v_i v_j, \quad D_{ijk} = V_0 B_{ijk}/v_i v_j v_k, \quad \ldots \qquad (12)$$

with v_i being the specific volume of component i. Note that D_{ij}, D_{ijk}, etc. are invariant with exchange of subscripts.

Equating eq 9 and 11 and substituting for $\mu_0 - \mu_0^0$ from eq 6, we obtain

$$\chi = \phi^{-2}\Big(\sum_{i=1}^{2}\sum_{j=1}^{2} E_{ij}\phi_i\phi_j + \sum_{i=1}^{2}\sum_{j=1}^{2}\sum_{k=1}^{2} E_{ijk}\phi_i\phi_j\phi_k + \ldots\Big) \qquad (13)$$

where

$$E_{ij} = (1/2)(1 - D_{ij}), \quad E_{ijk} = (1/3)(1 - D_{ijk}), \quad \ldots \qquad (14)$$

Considering that E_{ij}, E_{ijk}, etc. are invariant with exchange of subscripts, we may rewrite eq 13 as follows:

$$\chi = \xi_1^2(E_{11} + E_{111}\phi_1 + E_{1111}\phi_1^2 + \ldots) + \xi_2^2(E_{22} + E_{222}\phi_2 + E_{2222}\phi_2^2 + \ldots) + 2\xi_1\xi_2[E_{12} + (3/2)(E_{112}\phi_1 + E_{122}\phi_2) + 2E_{1112}\phi_1^2 + 3E_{1122}\phi_1\phi_2 + 2E_{1222}\phi_2^2 + \ldots] \qquad (15)$$

For $\xi_1 = 1$, χ should reduce to $\chi_{11}^{b}(\phi)$. Thus we find from eq 15

$$\chi_{11}^{b}(\phi) = E_{11} + E_{111}\phi + E_{1111}\phi^2 + \ldots \qquad (16)$$

Similarly, we obtain

$$\chi_{22}^{b}(\phi) = E_{22} + E_{222}\phi + E_{2222}\phi^2 + \ldots \qquad (17)$$

Hence, the first and second terms in eq 15 can be written $\xi_1^2\chi_{11}^{b}(\phi_1)$ and $\xi_2^2\chi_{22}^{b}(\phi_2)$, resectively. The sum multiplied by $2\xi_1\xi_2$ in eq 15 depends separately on ϕ_1 and ϕ_2 and can be taken as the contribution from all types of interactions between polymers 1 and 2 in our ternary solution. Thus it may be denoted by $\chi_{12}^{t}(\phi_1, \phi_2)$, i.e.,

$$\chi_{12}^{t}(\phi_1, \phi_2) = E_{12} + (3/2)(E_{112}\phi_1 + E_{122}\phi_2) + 2E_{1112}\phi_1^2 + 3E_{1122}\phi_1\phi_2 + 2E_{1222}\phi_2^2 + \ldots \qquad (18)$$

In this way, we arrive at

$$\chi = \xi_1^2\chi_{11}^{b}(\phi_1) + \xi_2^2\chi_{22}^{b}(\phi_2) + 2\xi_1\xi_2\chi_{12}^{t}(\phi_1, \phi_2) \qquad (19)$$

which is precisely what we wanted to derive, i.e., eq 8.

Discussion

Usually, on the basis of lattice-model considerations, χ for the ternary system concerned here is expressed as[2]

$$\chi = \xi_1\chi_{01}(\phi_1, \phi_2) + \xi_2\chi_{02}(\phi_1, \phi_2) - \xi_1\xi_2\chi_{12}(\phi_1, \phi_2) \qquad (20)$$

and χ_{ij} $(i, j = 0, 1, 2)$ is regarded as having something to do with the interaction between components i and j. However, this expression is of no practical use, because we have three unknown functions χ_{01}, χ_{02}, and χ_{12} for one experimentally measurable quantity χ. For this reason eq 20 is sometimes replaced by an empirical expression[3,4]

$$\chi = \xi_1\chi_{01}^{b}(\phi) + \xi_2\chi_{02}^{b}(\phi) - \xi_1\xi_2\chi_{12}^{*}(\phi_1, \phi_2) \qquad (21)$$

where χ_{0i}^{b} denotes the χ function for the binary solution of solvent 0 and polymer i. This expression enables us to estimate χ_{12}^{*} from measurement of $\chi(\phi_1, \phi_2)$, because both χ_{01}^{b} and χ_{02}^{b} can be determined by separate measurements on binary solutions. However, it differs from eq 19, the result from the present analysis, with respect to the coefficient and independent variable of each χ_{ii}^{b} (or χ_{0i}^{b}).[5] Thus, it is questionable whether χ_{12}^{*} so estimated truly reflects the interaction between polymers 1 and 2 in ternary solutions of the type considered. On the other hand, χ_{12}^{t} determinable by use of eq 19 is associated only with such interaction, as can be understood from its definition, and hence it should be more significant physically than χ_{12}^{*}.

References and Notes

(1) Kurata, M. *Thermodynamics of Polymer Solutions*; translated from the Japanese by H. Fujita, Harwood Academic: Chur, 1982.

(2) Koningsveld, R.; Chermin, H. A. G.; Gordon, M. *Proc. R. Soc. London, A* **1970**, *319*, 331. In this paper, the interaction function Ψ is defined in the Gibbs free energy by

$$\Psi = \phi_0\phi_1 g_{01}(\phi_1,\phi_2) + \phi_0\phi_2 g_{02}(\phi_1,\phi_2) + \phi_1\phi_2 g_{12}(\phi_1,\phi_2)$$

This expression gives the χ interaction function as eq 20 with χ_{0i} and χ_{12} defined by

$$\chi_{0i} = g_{0i} - \phi_0(\partial g_{0i}/\partial\phi),\ i = 1 \text{ or } 2$$

$$\chi_{12} = g_{12} + \phi(\partial g_{12}/\partial\phi)$$

(3) Kennedy, J. W. *A Specialist Periodical Report, Macromolecular Chemistry*, Bartholomew: Dorking, UK, 1980; Vol. 1, Chapter 14.

(4) Fukuda, T.; Nagata, M.; Inagaki, H. *Macromolecules* **1986**, *19*, 1411.

(5) One of the reviewers notified us that eq 21 can be rewritten as

$$\chi = \xi_1{}^2\chi_{01}{}^b + \xi_2{}^2\chi_{02}{}^b + \xi_1\xi_2(\chi_{01}{}^b + \chi_{02}{}^b - \chi_{12}{}^*)$$

when χ_{0i} and $\chi_{12}{}^*$ are composition-independent. Thus, a casual comparison of this equation with eq 19 suggests that

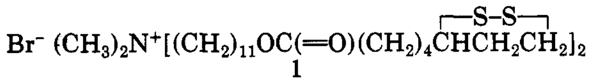
$$\chi_{ii}{}^b = \chi_{0i}{}^b,\ \chi_{12}{}^t = (\chi_{01}{}^b + \chi_{02}{}^b - \chi_{12}{}^*)/2$$

though physical meaning of the relations is an open question.

Communications to the Editor

pH-Triggered Vesicle Polymerization†

In this paper we show that surfactant vesicles derived from bis[11-(lipoyloxy)undecyl]dimethylammonium bromide (1) undergo rapid ring-opening polymerization,

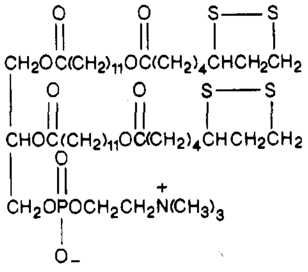


$$\mathrm{Br^{-}\ (CH_3)_2N^{+}[(CH_2)_{11}OC({=}O)(CH_2)_4\overset{\ulcorner S-S \urcorner}{CHCH_2CH_2}]_2}$$

1

when the pH of the dispersion is raised from 3.0 to 4.0. The pH-sensitivity of this polymerization affords a unique synthetic route to polymerized vesicles which should allow for the successful incorporation of highly sensitive comembrane components.

Phospholipid and surfactant vesicles serve as important models for biological membranes, as carriers of drugs, and as potential devices for solar energy conversion. While considerable progress has been made in the synthesis of polymeric analogues over the past 7 years,[1] new classes of polymerizable surfactants are needed, which will allow for milder polymerization conditions to be employed.[2] Recently, we have shown that vesicles composed of 1,2-bis-[12-(lipoyloxy)dodecanoyl]-*sn*-glycero-3-phosphocholine (2) can be polymerized via a ring-opening process at pH 8.5, using dithiothreitol (DTT) as an initiator.[3] In the course of examining the scope of lipoic acid based surfactants for polymerized vesicle synthesis, we discovered that vesicles made from 1 are rapidly and quantitatively polymerized when the pH is modestly raised from 3.0 to 4.0. This report details our preliminary findings.



2

Addition of 1.00 g (2.15 mmol) of bis(11-hydroxyundecyl)dimethylammonium bromide[4] to 50 mL of a 0.22 M dichloromethane solution of lipoic acid anhydride,[3] containing 0.57 g (4.7 mmol) of 4-(dimethylamino)pyridine, followed by (a) stirring for 24 h at room temperature under nitrogen, (b) filtering and concentrating the product mixture under reduced pressure, and (c) chromatographic purification (silica, $CHCl_3/CH_3OH$), afforded 1.66 g (92%) of 1 as a yellow oil.[5]

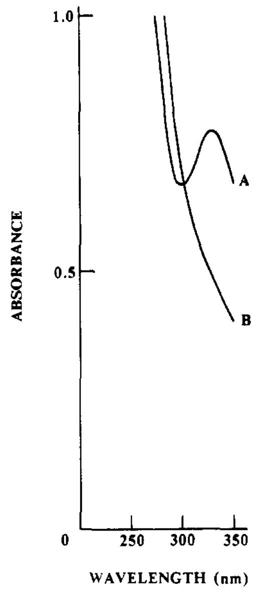


Figure 1. UV spectra of nonpolymerized (A) and polymerized (B) vesicles derived from 1.

Dispersal of 30 mg of 1 in 3 mL of 10^{-3} M HCl, by vortex mixing at room temperature, followed by 10 repetitive passes through a 0.1-μm Nuclepore membrane,[6] produced a vesicle dispersion ranging in diameter between 300 and 1300 Å (electron microscopy and dynamic light scattering).[3] Thin-layer chromatography (TLC), immediately after extrusion, indicated complete retention of the monomeric state. Upon standing for 7 h at 23 °C, approximately 50% of surfactant was converted into polymer (UV analysis[3]). In contrast, when the pH of the dispersion was raised from to 3.0 to 4.0 (or to pH 7.0), via addition of aqueous NaOH, *complete polymerization was observed within 1 min*, as indicated by the disappearance of the 1,2-dithiolane moiety (λ_{max} 330 nm, Figure 1) and by the retention of all of the surfactant at the origin of the TLC plate. Adjustment of the pH to 3.5 resulted in a 50% conversion to polymer after ca. 5 min.

Electron microscopic examination revealed no significant alteration in particle size after polymerization (Figure 2); light scattering also confirmed the retention of the size

---

† Supported by a grant from Kurita Water Industries, Ltd., Tokyo Japan.

0024-9297/87/2220-2029$01.50/0