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cast film could be doped to $Y = 0.13$ after 5-h exposure to iodine, while a single-crystalline specimen gave $Y = 0.026$ even after as long as 50-h exposure. Figure 3 also shows that the anisotropy in the conductivities $\sigma_{\parallel}/\sigma_{\perp}$ of the single crystal is 6.5 ± 0.4 and is independent of Y. This value of anisotropy is comparable to that reported by Schermann and Wegner[11] on dark conductivities of a single-crystalline poly(diacetylene) *p*-toluenesulfonic acid derivative (PDA–TS).

Recently, Siddiqui and Wilson[12] reported that the anisotropy for PDA–TS is $\sigma_{\parallel}/\sigma_{\perp} = 10^3$, which is in sharp contrast with the results obtained by Schermann and Wegner. They pointed out that Schermann and Wegner had used an undesirable arrangement of electrodes on the same face (surface electrodes), in which, when examining currents along the chains, the current must also flow in the directions perpendicular to the chains. This is not the reason for the low anisotropy of poly(4BCMU) single crystal, since we adopted evaporated-gold electrodes covering the edges of the specimen completely. Then, the difference in the anisotropy between poly(4BCMU) and PDA–TS single crystals might have resulted from the difference in their crystal forms. The single crystal of PDA–TS is known to be the most perfect among various poly(diacetylene)s, but poly(4BCMU) single crystal contains the disorder in the mutual level of the chains in the *c*-axis direction as above mentioned.[9] In addition, the nearest-neighbor distance of the chains for poly(4BCMU) is 0.533 nm in the direction of *a′* axis ($\sigma_{\perp}$ direction), which is much shorter than that of 0.75 nm for PDA–TS.[13] This evidence seems to give the reasons for the low anisotropy of poly(4BCMU) single crystal.

From the results given above, we may conclude as follows: (i) The conduction along the polymer chain is prevailing. (ii) The doping takes place mainly in the amorphous regions of the specimens. (iii) The dopant iodine is interacting with and providing charge carriers along the conjugated backbones of poly(4BCMU). (iv) Presumably the dopant may be acting also as bridges for hopping of charge carriers from one chain to another.

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Registry No. 5,7-Dodecadiyne-1,12-diol bis(*n*-butoxycarbonylmethyl)carbamate polymer, 68777-93-5; iodine, 7553-56-2.

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(1) Present address: Department of Materials Engineering, The Technological Univeristy of Nagaoka, Nagaoka, Niigata 949-54, Japan.
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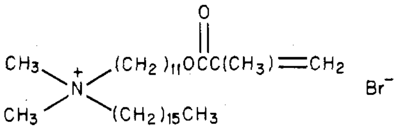
Degree of Polymerization of a Vesicle Membrane[1]

DURGADAS BOLIKAL and STEVEN L. REGEN*

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233. *Received September 13, 1983*

Polymerized vesicles are now receiving intense interest as stable models for biological membranes, as carriers of drugs, and as devices for solar energy conversion.[2–9] While considerable attention has focused on the synthetic design, gross morphology, entrapment efficiency, permeability, stability, and dynamic properties of such vesicles, surprisingly little effort has been aimed at characterizing the polymeric nature of the membrane.

In this paper, we report the molecular weight distribution of polymers formed within vesicles of dimethyl-*n*-hexadecyl[11-(methacryloyloxy)undecyl]ammonium bromide (1) via AIBN-induced and photoinduced polymerization.[10]



Results and Discussion

The preparation of polymerized and nonpolymerized vesicles derived from 1 has been previously described.[2] Characterization was made on the basis of Fourier transform ^{1}H NMR spectroscopy, turbidity, gel filtration behavior, electron microscopy, stability toward ethanol, and entrapment and permeability toward [^{14}C]sucrose. With use of similar preparative methods, a well-sonicated dispersion of 1 was prepared in distilled water and purified by gel filtration on a Sephadex G-50 column. The yield of vesicles, recovered in the void volume of the column, was ca. 95% (nitrogen analysis). After addition of a free-radical initiator (azobisisobutyronitrile, AIBN) and subsequent heating (80 °C), the resulting dispersion was purified by gel filtration (Sephadex G-50). Nitrogen analysis of the void-volume fraction revealed a 95% recovery of the vesicles. The dispersion was then freeze-dried to give a colorless solid (sample 1). In a second preparation, a similarly prepared aqueous dispersion of 1 was subjected to direct UV irradiation (254 nm, 0.5 h), gel filtered (95% recovery), and freeze-dried to give a colorless solid (sample 2). Both samples 1 and 2 were completely soluble in chloroform (nitrogen analysis) or chloroform containing 0.005 M tetrabutylammonium bromide and were analyzed directly by size-exclusion chromatography.

Elution profiles of samples 1 and 2 in pure chloroform depended significantly on the concentration of injected sample. In sharp contrast, analysis carried out with samples dissolved in chloroform containing 0.005 M tetrabutylammonium bromide yielded chromatograms that were independent of polymer concentration, in the range of 2.0–25.0 mg of polymer per milliliter of solvent. Increasing the salt concentration to 0.05 M had no influence on the elution profile. Retention volumes of polystyrene molecular weight standards (used to derive a universal calibration curve) in chloroform containing 0.05 M tetrabutylammonium bromide were identical with those found in pure chloroform.

Figure 1 reveals a substantial difference in apparent molecular weights between polymers formed from AIBN-initiated and photoinitiated polymerization; the former is substantially higher.[11] Measurement of the intrinsic viscosity of samples 1 and 2 together with these size-exclusion chromatography data and a universal calibration curve

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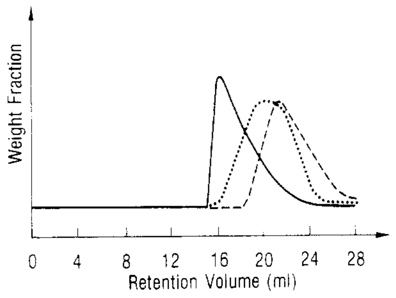

Figure 1. Typical size-exclusion chromatograms of sample 1 (solid curve), sample 2 (dashed curve), and sample 1, 80% transesterfied with CH_3OH (dotted curve). The elution volume of 1 is 29.5 mL.

allow for an estimation of the Mark–Houwink–Sakurada constants, K and α, using eq 1 and 2.[12] Here, η_1 and η_2

$$\frac{\eta_1}{\eta_2} = \frac{\sum_i w_{1i} J_i^{\alpha/(\alpha+1)}}{\sum_i w_{2i} J_i^{\alpha/(\alpha+1)}} \qquad (1)$$

$$\eta_1 = K^{1/(\alpha+1)} \sum_i w_{1i} J_i^{\alpha/(\alpha+1)} \qquad (2)$$

are the intrinsic viscosities of bulk samples 1 and 2, respectively, and w_{1i} and w_{2i} are the weight fractions of samples 1 and 2, respectively, of the ith species. The J_i values represent the product of the intrinsic viscosity and molecular weight for the ith species and are derived from the universal calibration curve together with the data in Figure 1. By use of the calculated values of $\alpha = 0.67$ and $K = 3.8 \times 10^{-3}$ mL/g, in combination with eq 3 and 4, the

$$\bar{M}_w = K^{-1/(\alpha+1)} \sum_i w_i J_i^{1/(\alpha+1)} \qquad (3)$$

$$\bar{M}_n = K^{-1/(\alpha+1)} / \sum_i w_i J_i^{-1/(\alpha+1)} \qquad (4)$$

estimated weight-average ($\bar{M}_w$) and number-average ($\bar{M}_n$) molecular weights for sample 1 are 3.7×10^6 and 3.98×10^5, respectively; for sample 2, $\bar{M}_w = 3.5 \times 10^5$ and $\bar{M}_n = 7.93 \times 10^4$. On the basis of $\bar{M}_n$ for samples 1 and 2, the average number of monomers contained in these polymers is estimated to be 677 and 135, respectively.[13,14] Upon extended UV irradiation (2 h), $\bar{M}_n$ and $\bar{M}_w$ for sample 2 decreased to 5.5×10^4 and 1.4×10^5, respectively, indicating that the polymerized surfactant is susceptible to photodegradation.

The absolute value of the calculated molecular weights reported herein must be regarded as approximate because of error resulting primarily from (a) deviation from ideal size-exclusion chromatographic behavior and (b) possible aggregation due to charge clustering.[15] Several lines of evidence, however, indicate that both of these factors do not contribute significantly to the observed elution profiles. First, successive injections of polymer samples gave reproducible chromatograms. This result, together with the fact that monomer 1 elutes within the expected molecular weight range of a polystyrene calibration curve, strongly suggests that polymer adsorption onto the stationary phase is negligible. Second, as mentioned above, elution profiles were independent of polymer concentration. This finding implies that polymer aggregation is minimal. Third, size-exclusion chromatographic separation of apparent high and low molecular weight components of sample 1, followed by reinjection and analysis, produced well-defined and distinct polymer fractions (Figure 2). All of these observations, taken together, provide strong evidence that adsorption and polymer aggregation effects are minimal under the chromatographic conditions used. Finally, in an effort to convert sample 1 into conventional poly(methyl methacrylate), transesterification in methanol was attempted under acidic and basic conditions (see Experimental Section). In both cases polymers were produced having ca. 20% residual pendant surfactant groups. Repeated transesterification failed to alter the polymer composition. Size-exclusion chromatography of the resulting polymer (Figure 1) yields an apparent number-average molecular weight of 1.25×10^5 (based on a polystyrene calibration curve) which corresponds to an average of 633 monomer units per polymer chain. This value is in excellent agreement with the average chain length calculated for sample 1.

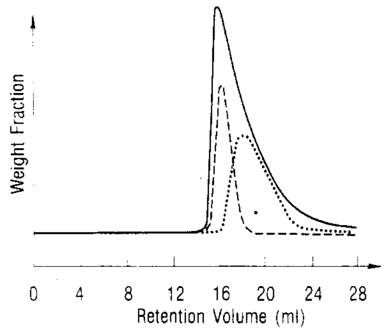

Figure 2. Size-exclusion chromatograms of sample 1 (solid curve), a high molecular weight fraction of sample 1, reinjected (dashed curve), and a low molecular weight fraction of sample 1, reinjected (dotted curve). The elution volume of 1 is 29.5 mL.

Experimental Section

Size-Exclusion Chromatography. All size-exclusion chromatography measurements were made on a Waters ALC/GPC-201 instrument equipped with a Model 6000 A solvent delivery system, a differential refractive index detector, a U6K injector, and a combination of 10^5- and 10^4-Å Microstyragel and 10^3-Å Ultrastyragel columns (30 cm × 7.8 mm) connected in series. Polystyrene molecular weight standards used were 3×10^6, 6.3×10^4, 3.5×10^4, 9.0×10^3, and 2.9×10^3. The following conditions were routinely employed: solvent, $CHCl_3$ containing 0.005 M tetrabutylammonium bromide; pressure, 600 psi; flow rate, 1.0 mL/min; sample concentration, 0.01 g/mL; sample size, 100 μL. Hydrodynamic volumes were taken into account in establishing the universal calibration curve.[16] Samples were prepared for size-exclusion chromatography by (a) freeze-drying the polymerized vesicle dispersion (5 mg of sample 1 in 0.5 mL of water), (b) dissolving the polymer in 0.5 mL of $CHCl_3$ containing tetrabutylammonium bromide, and (c) filtering the resulting solution through a 0.5-μm Millipore filter.

Polymerized Vesicles of 1. Typically, 5 mg of 1 plus 0.5 mL of distilled water were vortex mixed under a nitrogen atmosphere for 5 min at room temperature, followed by sonication (Heat Systems Model W-225 R, bath type, 50 °C) to constant turbidity. Vesicle dispersions of 1, before and after polymerization, were purified by passage through a Sephadex G-50 column (2.0 g of Sephadex (dry weight) contained in a 1.0 × 50 cm glass column) using pure water as the eluent. The yield of vesicles recovered in the void volume of the column exceeded 90% in all cases, on the basis of nitrogen analysis.[17,18]

Photopolymerization. A dispersion of 1 was placed in a 13 × 100 mm Vycor tube and degassed with a slow stream of nitrogen for 2 min. The tube was then sealed with a No-Air stopper, placed inside the Rayonet photoreactor, and irradiated for 0.5 h.

AIBN-Induced Polymerization. Typically, 0.1 mg of solid AIBN was added directly to a well-sonicated dispersion of 1 followed by additional sonication for 5 min at 50 °C. The resulting mixture was degassed with nitrogen for 2 min and placed in a constant-temperature bath maintained at 80 °C for 14 h. In the absence of AIBN, no polymerization occurred.

Size-exclusion chromatograms, obtained by using pure chloroform as the eluting solvent, indicated that the extent of polymerization in all cases (photopolymerization and AIBN-induced polymerization) exceeded 90%.

Transesterification of Sample 1. A freeze-dried sample of sample 1 (200 mg) was dissolved in 20 mL of methanol and heated with 0.15 mL of concentrated H_2SO_4 for 24 h at 100 °C. Upon cooling (15 °C), the transesterified polymer precipitated from solution and was isolated by centrifugation. The polymer was washed with cold water (2 × 5 mL) and dried [12 h, 22 °C (0.01 mm)], affording 100 mg of a product containing 1.7% nitrogen. Repeated transesterification of the recovered polymer, five times in succession, resulted in a nitrogen content of 1.4, 1.2, 1.1, 1.1, and 1.1%, respectively. A value of 1.1% corresponds to a level of transesterification equaling ca. 85%. ^{1}H NMR analysis ($CDCl_3$) of the transesterified polymer confirmed the presence of the methoxy moiety of δ 3.7. Integration of the methoxy band relative to absorption bands due to CH_2N^+ and CH_3N^+ protons yielded an estimate of the extent of transesterification equaling ca. 75%. On the basis of nitrogen and ^{1}H NMR analyses, the extent of transesterification is estimated to be 80 ± 5%. Similar transesterification carried out under basic conditions ($KOCH_3$) resulted in a polymer which also could not be exchanged beyond ca. 80%.

Viscosity Measurements. Viscosities were determined at 25 ± 0.1 °C in $CHCl_3$ containing 0.005 M tetrabutylammonium bromide. Intrinsic viscosities determined for samples 1 and 2 were 87.5 and 12.1 mL/g, respectively.

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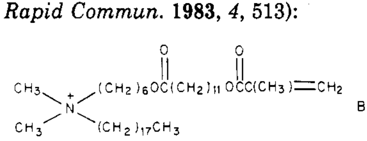
(10) Very recently, Dorn et al. have reported polystyrene equivalent molecular weights for polymers formed within bilayer vesicles comprised of the following lipid (Dorn, K.; Patton, E. V.; Klingbiel, R. T.; O'Brien, D. F.; Ringsdorf, H. *Makromol Chem., Rapid Commun.* **1983**, *4*, 513):



(11) In sharp contrast to vesicle dispersions, homogeneous solutions of 1 in benzene (10 mg/mL) show no evidence of polymerization after 16 h at 80 °C in the presence of AIBN (0.1 mg/mL). We presume that the inability to polymerize 1 under these conditions is due to its very low concentration. In contrast, the "effective concentration" of 1, in vesicle form, is extremely high.

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(13) The radii, of polymerized vesicles of 1, determined from electron microscopy,[2] ranged between 100 and 350 Å. If we assume that (1) all of the vesicles are unilamellar, (2) the bilayer thickness is similar to that of saturated phospholipids, i.e., 50 Å thick, and (3) each lipid occupies an area of 70 Å^2, then the calculated number of lipids per vesicle is 2×10^3 to 4×10^4. This crude estimate implies that there are, to a first approximation, 3–60 polymer chains per AIBN-polymerized vesicle and 15–300 chains per UV-polymerized vesicle (see ref 10 for similar estimates).

(14) Interestingly, polymerization of large multilamellar dispersions of 1 (vortex mixed, but not sonicated) using similar procedures, afforded polymers of lower molecular weight; specific values of $\bar{M}_n$ and $\bar{M}_w$ were 8.5×10^4 and 1.1×10^6 for AIBN-induced polymerization and 5.4×10^4 and 2.1×10^5 for UV (0.5 h) polymerization. We have, at present, no clear understanding of this behavior.

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Comment on the Correct Polarization Factor for Light Scattering Photometers Employing Annular Detection

PAUL S. RUSSO,*† MATTHEW BISHOP,†
KENNETH H. LANGLEY,‡ and FRANK E. KARASZ†

Polymer Science and Engineering Department and
Department of Physics and Astronomy, University of
Massachusetts, Amherst, Massachusetts 01003.
Received January 13, 1983

Many types of photometers have been described for the measurement of scattered light. For studies of dilute polymer solutions, the mainstay has been the conventional goniometer, in which the detector physically rotates about the sample in a horizontal plane (Figure 1a). Both conventional and laser sources have been used. Over the past few years, a device employing a laser source and small-angle annular detection has become popular. Pioneered in the early 1970s by Kaye, McDaniel, and Havlik (KMH),[1-3] the annular design (Figure 1b) is available commercially as the Chromatix (LDC-Milton Roy) KMX-6.

In both types of photometer, factors are applied to the measured signal to correct for the effects of scattering geometry and incident beam polarization at a given scattering angle. Geometrical and polarization factors for the conventional goniometer are well-known.[4-6] While the geometric corrections for the annular device have received much attention in ref 1–3 and in the Chromatix KMX-6 instruction manual,[7] the polarization factors for the annular device are merely stated, with little supporting development. This, together with their resemblance to those for a conventional goniometer using an unpolarized incident beam, has recently led to the contention[8] that the polarization factors given by KMH and Chromatix must be incorrect. Our purpose in this brief note is to resolve this issue by developing in adequate detail the correct polarization factors for the increasingly popular annular type of instrument. We shall see that factors originally presented by KMH are correct.

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† Polymer Science and Engineering Department.

‡ Department of Physics and Astronomy.

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