and thus invalidates our eq A21. The problem under discussion pertains to a special case of the treatment of thermodynamics of copolymerization outlined by Szwarc and Perrin,[1] namely, to the needed modification of the treatment when the matrix **M** is singular ($|\mathbf{M}| = 0$). Since the general treatment utilizes in the calculation the reciprocal of **M**, and a singular matrix has no reciprocal, one of the four equations leading to the solution is lost and has to be replaced by a proper alternative relation. Since eq A21 given at the end of Appendix II of ref 1 is erroneous, as pointed out by Szymanski, it is necessary to derive a correct fourth equation for our scheme in order to determine the unknown ${}^\circ A_1$ and ${}^\circ B_1$. The problem is even broader. In the case of a singular matrix **M** a novel approach is needed to allow determination of the proportion of A and B units in the first segments of each of the n-mers.

As shown in the original paper,[1] for $|\mathbf{M}| = 0$ the equilibrium probabilities for finding A and B in any segment of any n-mer ($n > 1$), except for the first and the last, are constant and independent of i and the nature of the preceding unit. These probabilities are again constant and independent of the preceding units for the last segments of the n-mers ($n > 1$), although different from the previous ones.

Denote by ${}^\circ A_i$ and ${}^\circ B_i$ the equilibrium numbers of A's and B's in the first segments of i-mers. These are subject to the following conditions: $\sum {}^\circ A_i = A_0$, $\sum {}^\circ B_i = B_0$, and ${}^\circ A_i + {}^\circ B_i =$ constant, where the constant depends on i. A_0 and B_0 denote the initial numbers of XA* and XB* (the initiators) introduced at the onset of the reaction. Any arbitrary variation of ${}^\circ A_i$ and ${}^\circ B_i$ that does not violate the above conditions leaves the total free energy of the bonds unchanged, because for $|\mathbf{M}| = 0$, i.e., for $K_{11}K_{22} = K_{12}K_{21}$, we have $G(\text{A–A}) + G(\text{B–B}) = G(\text{A–B}) + G(\text{B–A})$. Hence equilibrium is attained when the distributions of ${}^\circ A_i$ and ${}^\circ B_i$, subject to the above-stated conditions, are at maximum probability; i.e.

$$\delta[(A_0 + B_0)!/\Pi {}^\circ A_i! \Pi {}^\circ B_i!] = 0$$

still subject to the above-stated conditions. The Lagrange method of undetermined multipliers, combined with the Stirling approximation, leads to the results

$${}^\circ A_1/{}^\circ B_1 = {}^\circ A_2/{}^\circ B_2 = {}^\circ A_3/{}^\circ B_3 = \dots = A_0/B_0$$

thus providing the desired solution of the equilibrium problem for the special case of singular matrix **M**.

Added Note: Equations 18 and 19 of ref 1 should have the "inverse" (i.e., -1) omitted.

References and Notes

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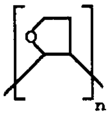
Communications to the Editor

Ring Opening of Poly(2,3-tetrahydrofurandiyl)[1]

Polymers derived from poly(1,2-disubstituted ethylenes) are typically difficult to obtain by polymerization of the double bond. Alkenyl ethers are a notable exception. A possible approach to synthesis of poly(1,2-disubstituted ethylenes) is to polymerize an alkenyl ether containing functional groups that allow transformation to a variety of products. We report that poly(2,3-tetrahydrofurandiyl) (**1**), a poly(alkenyl ether), has been modified to produce copolymers containing unusual 1,2-disubstituted ethylene units by direct transformation of the cyclic repeat unit.



1

poly(2,3-tetrahydrofurandiyl)

Polyether **1** may be obtained by the polymerization of 2,3-dihydrofuran at low temperature in bulk or in solution, using boron trifluoride gas or boron trifluoride etherate as initiator.[2-4] Treatment of **1** with concentrated hydriodic acid has been found to give partial conversion to a ring-opened product containing iodine, which, in turn, may be converted to an acetate.

Reaction of 1 with Hydriodic Acid. **1** was prepared by the polymerization of 2,3-dihydrofuran with boron trifluoride etherate initiator, using anhydrous conditions, an Ar atmosphere, and a dry ice–2-propanol bath for temperature control. After 48 h the polymerization was quenched with methanol followed by concentrated ammonia. The polymer was precipitated twice into methanol from methylene chloride, dried in vacuo, and stored in a freezer, under nitrogen, stabilized with 0.5 wt % Ultranox 626 (Borg-Warner) and 0.5 wt % Ultranox 236 (Borg-Warner) inhibitors until use.

Polymer **1** (1.00 g) was dissolved in 50 mL of 55–57% hydriodic acid (distilled as the azeotrope from 47% solution) by stirring them together at room temperature. The reaction flask was equipped with a gas inlet and a reflux condenser with a gas outlet. During the dissolution period, Ar was bubbled into the liquid for 20 min, and then Ar was used to sweep the reaction flask. The solution was brought to 62 °C and held at that temperature for 12 h. After cooling to room temperature, the mixture of red-brown solution and red-brown solid was slowly added to a slight excess of aqueous potassium bicarbonate at ice-bath temperature. The solid was collected by suction filtration and washed with methanol. The solid was dissolved in tetrahydrofuran, stirred for 10 min over a small amount of potassium bicarbonate, filtered through glass wool, and precipitated into methanol. The solid was collected by suction filtration, washed with methanol, and dried in vacuo to leave 1.31 g of light yellow solid **2**: IR (film, all bands were broad) 3445, 2965, 2940, 2865, 1434, 1225, 1057, 922, 689 cm^{-1}; ^{1}H NMR (CDCl$_3$, (CH$_3$)$_4$Si, all peaks were broad) 3.8, 3.4–3.0, 2.4, 1.9 ppm; ^{13}C NMR (25.178 MHz, CDCl$_3$, (CH$_3$)$_4$Si, all peaks were broad) 84.1, 81.0, 79.8, 68.0, 67.1, 47.8, 44.2, 33.1, 30.2, 29.8, 26.9, 6.9 ppm. Elemental analysis of **2** yielded 53.81% C, 6.82% H, and 23.19% I, which corresponds to a conversion of one out of six repeat units to the monoiodide form (assuming no diiodide units). However, it is not possible on the basis of these data to

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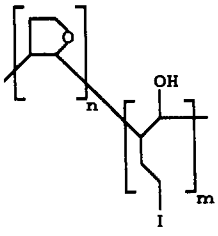
Table I
Intrinsic Viscosity[a] of Starting Material and Products

polymer	intrinsic viscosity, dL/g
1	1.4
2	0.34
3	0.62

[a] Tetrahydrofuran, 25.00 °C, Ubbelohde viscometer.

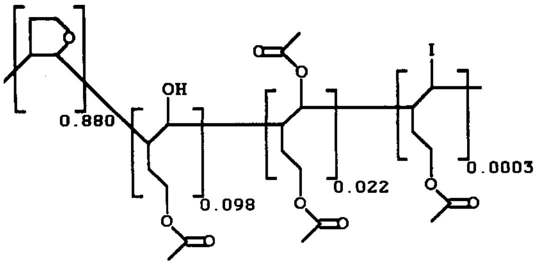
exclude the possibility of the formation of ~2–3% of diiodo repeat units.



2

Reaction of 2 with Potassium Acetate. Polymer **2** was used without further purification. ACS grade potassium acetate and dimethylformamide were used as received.

Polymer **2** (0.896 g) was dissolved by stirring with 90 mL of dimethylformamide in a reaction flask fitted with a gas inlet and a reflux condenser with a gas outlet. Potassium acetate (12.54 g) was added to the solution, and Ar was bubbled into the liquid for 0.5 h. The reaction flask was then swept with Ar and placed in a boiling water bath for 1 h. The resulting mixture of white solid and light-brown liquid was cooled to room temperature and filtered through a glass frit. The white solid was thoroughly washed with DMF, and the filtrate was poured into excess water to form a foamy, white precipitate. The precipitate was collected by suction filtration, washed with water, and air-dried. The solid was dissolved in methylene chloride, filtered through glass wool, and precipitated into methanol. The precipitate was collected by suction filtration, washed with methanol, and dried in vacuo to yield 0.611 g of hard, brown solid, **3**. Repeated precipitation and extended extraction with acetone yielded a faintly yellow solid: IR (film, all bands were broad) 3455, 2965, 2945, 2875, 1730, 1448, 1368, 1239, 1055, 926, 699 cm^{-1}; ^{1}H NMR (CDCl$_3$, (CH$_3$)$_4$Si, all peaks were broad) 4.2, 3.8, 2.4, 2.0, 1.9 ppm; ^{13}C NMR (25.178 MHz, CDCl$_3$, (CH$_3$)$_4$Si, most peaks were broad) 171.0, 84.1, 81.1, 79.8, 67.9, 67.6, 66.9, 64.2–62.8, 47.8, 47.4, 45.5, 44.1, 42.0, 30.3, 29.7, 27.0, 21.0 ppm. Elemental analysis of **3** yielded 65.77% C, 8.27% H, and 0.047% I. Assuming that the value for iodine content represents unreacted iodide in the polymer (either primary or secondary) and that approximately 2% of diiodo units were originally formed in **2**, this analysis is consistent with a random distribution of the structural units shown below.



3

Results and Discussion. Although secondary iodide units might be expected to form in the conversion of **1** or **2**, they are apparently only formed at ~2% levels. No evidence of the primary alcohol groups that might accompany the secondary iodide functions was observed in the carbon NMR spectrum, nor were secondary iodide groups directly observed. On the other hand, evidence of secondary alcohol units was observed in the carbon NMR spectrum in deuteriobromobenzene (^{13}C (bromobenzene-d_5, HMDSO) 73.5 ppm for the hydroxyl group on the methine carbon atom) and was also evident from the elemental analytical data for **3**. (A less intense peak at 71.0 ppm may be caused by secondary hydroxyl groups in different stereochemical environments.) Attached-proton-test (APT) carbon NMR[5] experiments were performed and showed the peaks at 33.1 and 6.9 ppm to be from methylene carbon atoms. The peak at 6.9 ppm is assigned as primary iodide. The degree of conversion of **1** to **2** is approximately 16–18% by integration of the proton NMR spectrum. Insolubility of the reaction product after partial conversion is a likely reason for the incomplete reaction. The product **2** is unstable and both eliminates HI and cross-links if allowed to stand over a period of days at room temperature.

Treatment of **2** with potassium acetate to form **3** apparently converts the iodide units nearly completely to acetate groups. The set of peaks at 3.43–3.0 ppm in the proton spectrum of **2**, corresponding to protons α to the iodide group, almost completely disappears and is replaced with peaks at 4.2 (CH_2O-Ac) and 2.0 ppm (C(O)CH$_3$). A single set of acetate peaks appears in the carbon NMR spectrum of **3** at 171.0 and 21.0 ppm. There is little evidence of elimination in the conversion of **2** to **3**, the dominant reaction being the substitution of acetate for iodide units.

Intrinsic viscositites of **1**, **2**, and **3**, measured with an Ubbelohde viscometer at 25.00 °C in tetrahydrofuran, are shown in Table I. What is most dramatic is the large decrease in intrinsic viscosity in going from **1** to **2**. Because the reaction is a ring-opening reaction, **2** is expected to be much more flexible than **1** and should show lowered viscosity. Efforts to determine if the molecular weight of **1** is decreased upon conversion to **2** and **3** are in progress.

The iodide **2**, although unstable, is a potential source for many 1,2-disubstituted ethylene copolymer derivatives: the acetate formed from it provides an example of an unusual, highly substituted repeat unit. In conclusion, we have demonstrated that the cyclic repeat unit polymer poly(alkenyl ether) (**1**) is transformable to a polymer containing acyclic units with interesting functionality. Work to expand the scope of this transformation as well as to increase the extent of modification is continuing. Direct analytical techniques that will permit confirmation of the presence of diiodide repeat units are being investigated.

Acknowledgment. Partial support of this work in the form of a fellowship to R.W. was granted by the Goodyear Foundation and is gratefully acknowledged.

Registry No. 1 (SRU), 79346-83-1; 1 (homopolymer), 75454-45-4; HI, 10034-85-2.

References and Notes

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Received May 22, 1986

Dynamical Properties of High Molecular Weight Polystyrene in Cyclopentane at the Θ Temperature

This communication is prompted by an apparent inconsistency between recently reported results[1-3] for the dynamical behavior of polystyrene (PS) in semidilute Θ solutions. Such systems have been treated theoretically by Brochard and de Gennes.[4,5] Hecht et al.[1] reported the relationship

$$D \sim C^{0.94\pm0.08}$$

where the quasi-elastic light scattering (QELS) measurements were made on a PS of $\bar{M}_w = 2.6 \times 10^7$ ($\bar{M}_w/\bar{M}_n = 1.30$) dissolved in cyclohexane at 34 °C. D was evaluated by using a two-parameter cumulant fit. It was inferred that the time scale of the measurements corresponded to that at which the semidilute solution behaves as a viscous fluid (i.e., $\Gamma T_R < 1$, where Γ is the relaxation rate and T_R is the lifetime of the interchain entanglements characterizing the transient network.[4,5] Adam and Delsanti[2] have also described measurements on the same system on a similar time scale but for samples of much lower molecular weight ($M < 10^6$). They found that D (evaluated by using a single-exponential fit to the QELS data) increased linearly with increasing concentration:

$$D_c\ (\mathrm{cm^2\ s^{-1}}) = 1.25 \times 10^{-6} C^1$$

In addition, Adam and Delsanti analyzed the structure factor for higher molecular weight samples in terms of a bimodal model, on a time scale at which the solution behaves as a gel. At the shortest times, a q^2-dependent relaxation (termed the gel diffusion coefficient) was separated, and this quantity was also found to be linearly dependent on concentration. At the longest times, a q-independent structural relaxation was obtained.

Subsequently, Brown[3] analyzed the dynamic structure factor obtained in semidilute Θ solutions of high molecular weight PS ($\bar{M}_w = 8 \times 10^6$ and 15×10^6) in cyclopentane at 21 °C. On short time scales (gel regime), a bimodal model with a floating base line was used to describe the data, and two q^2-dependent modes were resolved. The fast component was observed to be concentration independent at modest semidilute concentrations up to $15C^*$ (using $C^* = 3M/4\pi R_g{}^3 N_A$, a finding that agrees with the theoretical prediction of Brochard.[5] However, the slow component was noted to *decrease* with increasing concentration, in conflict with the results described in ref 1 and 2. This unsatisfactory situation stimulated us to further examine the PS/cyclopentane system using the same sample ($\bar{M}_w = 15 \times 10^6$) but extending the measurements over a much wider range of concentration and a broad span of angles.

The experimental details and the data analysis are as described previously.[3] Great care was taken to ensure solution homogeneity. These were prepared by concentrating optically clear solutions in a dust-free atmosphere by very slow evaporation. The 10-mm NMR tubes were then flame-sealed at −15 °C and placed in an oven at 50 °C for 6 months to achieve homogeneity; the data shown in Figure 1A were obtained by using a three-cumulants fit.

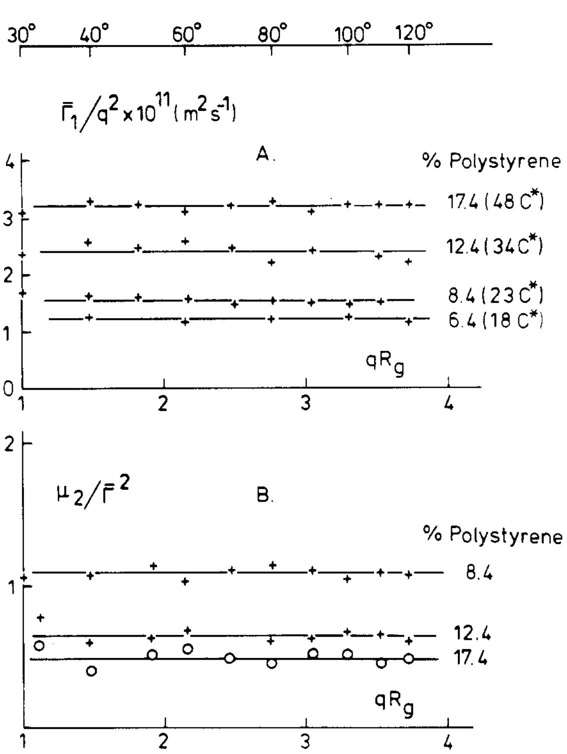

Figure 1. (A) Initial decay rate (Γ_1/q^2) as a function of qR_g for polystyrene ($\bar{M}_w = 15 \times 10^6$) in cyclopentane at the Θ temperature (21 °C) at a series of concentrations in the semidilute regime. C^* is defined as $C^* = 3M/4\pi R_g{}^3 N_A$. (B) Values of the normalized second cumulant, μ_2/Γ^2, corresponding to the data in (A).

Over the angular range 30–120° the first cumulant (Γ_1/q^2) is independent of q. This is the behavior anticipated in the semidilute region with parameters corresponding to the hydrodynamic regime (i.e., macroscopic displacements in the range $q\xi < 1$, where ξ is the dynamic correlation length). In poor solvents, where the radius of gyration, R_g, is small, the crossover to q^3 behavior will be accessible only at very much lower concentrations at high angles.

Figure 1B shows the normalized second cumulant as a function of qR_g at a series of concentrations. This parameter is large but decreases with increasing concentration at a given angle. The probable root of this behavior is the increasing dominance of the gel mode at the expense of translational motions at the higher concentrations.

Figure 2 presents the results of a discrete multiexponential analysis in terms of two frequency components. The slopes yield the following: curve A, $D_g = (\Gamma_g/q^2)$; curve B, $D_s = (\Gamma_s/q^2)$; curve C, $\bar{D}_{\mathrm{cum}} = (\Gamma_1/q^2)$. These data suggest that both fast and slow components may be diffusive in character, although the slower mode has a proportionally greater uncertainty, the error bars denoting the 95% confidence interval. We note that this interpretation differs from that of Adam and Delsanti,[2] who resolved their data into q^2-dependent and q-independent quantities, depending on the sampling time.

Figure 3 shows the concentration dependence of the two diffusion coefficients. Each point of this diagram was obtained as the slope of a plot over the angular range 30–120° as shown in Figure 2. The curve for the gel mode (curve A) at the higher concentrations corresponds to $D_g \sim C^1$. A similar result is found for the cumulant-evaluated data (curve B). However, $\Gamma T_R < 1$ will, in general, only be realized with modest molecular weights ($M < 10^6$), as emphasized in ref 2. With higher M and usual measurement parameters, the quantity $\bar{D}_{\mathrm{cum}}$ will inevitably be a mixture of contributions from different relaxational modes and will be difficult to interpret. The exponent of unity

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