well beyond the gel point, were never available in greater than 2-5-mg quantities. The viscosity of each sample was thus measured at four different concentrations, by appropriate careful dilution within the viscometer, with fresh prefiltered solvent. Extreme care was exercised to keep the solutions and equipment dust-free during the measurements.

Molecular weights were measured by injecting 250-500 μL of approximately 1-2% w/v of the above solutions into a KMX-6 Chromatix GPC/LALLS photometer equipped with six μStyragel (Waters Associates) columns of porosity varying between 10^5 and 100 Å.

Registry No. (BTA)(DMG) (copolymer), 34606-50-3.

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Equilibrium Copolymerization

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In a recent paper Szwarc and Perrin[1] discussed equilibrium copolymerization in living polymer systems. In their treatment, which correctly allows detailed calculations of all the properties of such systems, they used a matrix **M**

$$\mathbf{M} = \begin{pmatrix} K_{11}a & K_{21}a \\ K_{12}b & K_{22}b \end{pmatrix}$$

where *K*'s denote the equilibrium constants of reactions such as $A_n{}^* + A \rightleftharpoons A_nA_{n+1}{}^*$, $A_n{}^* + B \rightleftharpoons A_nB_{n+1}{}^*$, etc. The symbols *a* and *b* are the equilibrium concentrations of the respective monomers, and $A_n{}^*$, $B_n{}^*$, $A_nA_{n+1}{}^*$, and $A_nB_{n+1}{}^*$ are the equilibrium concentrations of living *n*-mers terminated by A and B and living $(n + 1)$-mers terminated by diads AA and AB, etc., respectively.

In the special case of a singular matrix **M**, i.e., for $|\mathbf{M}| = 0$, its reciprocal does not exist, and the treatment has to be modified. The modified treatment is discussed at the end of Szwarc and Perrin's Appendix II. It reveals that for $|\mathbf{M}| = 0$, the probabilities for finding the units A or B in any *n*-mer, $n > 1$, are constant for all *n*-mers and all segments but the first and last. The probabilities are again constant, independent of $n > 1$, for the last segments, although their values differ from the previous ones, whereas the probabilities for A or B being in the first segments of *n*-mers (including $n = 1$) remain undefined. In an attempt to get the latter probabilities, Szwarc and Perrin wrote eq A20 as

$$\mathbf{M}\begin{pmatrix} ^\circ A_1 \\ ^\circ B_1 \end{pmatrix} = \begin{pmatrix} A_2{}^* \\ B_2{}^* \end{pmatrix} = \mathbf{N}'\begin{pmatrix} ^\circ A_1 \\ ^\circ B_1 \end{pmatrix}$$

whereas the correct form is

$$\mathbf{M}\begin{pmatrix} ^\circ A_1 \\ ^\circ B_1 \end{pmatrix} = \begin{pmatrix} A_2{}^* \\ B_2{}^* \end{pmatrix} = \mathbf{N}'\begin{pmatrix} ^\circ A_2 \\ ^\circ B_2 \end{pmatrix}$$

where $^\circ A_1$ and $^\circ B_1$ denote the equilibrium concentrations of the initiating 1-mers, $^\circ A_2$ and $^\circ B_2$ the equilibrium concentrations of the *dimers* starting with A and B, respectively, and $A_2{}^*$ and $B_2{}^*$ the equilibrium concentrations of the dimers terminated by the corresponding units. This error invalidates their last equation (eq A21), needed for solution of the problem. It is necessary, therefore, to derive the correct method yielding the probabilities for *A* and *B* in the first segments of the polymers.

The author of this note presented a simple solution[2] of equilibrium copolymerization for high degrees of polymerization ($\overline{\mathrm{DP}}_n \rightarrow \infty$). This solution may be applied also to the case when $|\mathbf{M}| = 0$, provided $\overline{\mathrm{DP}}_n$ is high. However, it gives no access to values such as concentrations of *n*-mers and their microstructure.

Therefore, one of the equations from ref 2, e.g., the relation equating the concentrations of diads AB and BA

$$(a_0 - a)(1 - K_{11}a) = (b_0 - b)(1 - K_{22}b) \qquad (1)$$

(where a_0 and b_0 are the starting concentrations of the respective comonomers) can be used (after replacing the erroneous (A20) and (A21)) to get the approximate solution of Szwarc and Perrin's equations when $|\mathbf{M}| = 0$. The solution would be only approximate because (1) is valid only for $\overline{\mathrm{DP}}_n \rightarrow \infty$ and the difference between the concentrations of heterodiads is especially important for low $\overline{\mathrm{DP}}_n$.

References and Notes

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Reply to the Preceding Note. Solution of the Equilibrium Copolymerization Equations for the Case of the Singular Matrix M

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Dr. Szymanski is correct. The next to last equation (eq A20) of our paper[1] is erroneous. It reads

$$\mathbf{M}\begin{pmatrix} ^\circ A_1 \\ ^\circ B_1 \end{pmatrix} = \begin{pmatrix} A_2{}^* \\ B_2{}^* \end{pmatrix} = \mathbf{N}'\begin{pmatrix} ^\circ A_1 \\ ^\circ B_1 \end{pmatrix}$$

instead of the correct

$$\mathbf{M}\begin{pmatrix} ^\circ A_1 \\ ^\circ B_1 \end{pmatrix} = \begin{pmatrix} A_2{}^* \\ B_2{}^* \end{pmatrix} = \mathbf{N}'\begin{pmatrix} ^\circ A_2 \\ ^\circ B_2 \end{pmatrix}$$

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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.

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

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

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

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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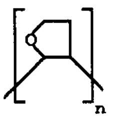
Communications to the Editor

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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