um(II) couples and their reactivity toward outer-sphere oxidants and estimated a k of electron transfer in such systems of less than or equal to 10^5 mol^{-1} dm^3 s^{-1}.

Conclusions

The present data show two interesting features: (a) that $Ru(bpy)_3^{2+}$ by virture of its luminescence spectrum and excited-state lifetime can be used as a monitor of the rigidity of the medium and (b) that cellophane provides a very convenient matrix whose properties change only monotonously without any discontinuity for the temperature range from 77 K to room temperature. Cellophane provides a medium where no translational motion of the compound absorbed in cellulose is observed. Also, data show that the $Ru(bpy)_3^{2+}$ excited-state quenching by $CrCl_3$ is mainly energy transfer in nature and that electron transfer only takes place when the reacting species are in close proximity. The rate constant for electron transfer is more than 2 orders of magnitude smaller than the rate constant for energy transfer. However, the relative ratio, or the extent of the two reactions, depends quite markedly on the viscosity of the medium.

Acknowledgment. We thank the National Science Foundation for support of this work via Grant No. CHE 82-01226. Our thanks are also due to Dr. James A. Wheeler for writing the computer programs used to fit the experimental data.

Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; Cr(III), 16065-83-1; cellulose, 9004-34-6; glycerol, 56-81-5; water, 7732-18-5.

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Structural Isomerism in Polycondensates. 2. Aspects for Monomers with Independent Functional Groups

Ulrich W. Suter* and Piero Pino

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Institut fuer Polymere, Eidgenoessische Technische Hochschule Zuerich, CH-8092 Zuerich, Switzerland. *Received October 12, 1983*

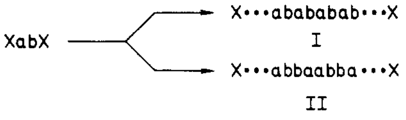
ABSTRACT: Structural isomerism and the possibility to steer structural regularity in homo- and bipolycondensates from at least one homobifunctional nonsymmetric monomer obtained in one kinetically controlled synthetic step are investigated theoretically. The probability of two adjacent nonsymmetric units in a chain to point in the same direction, s, is used to quantify structural regularity. A difference in reactivity between the functional groups of the nonsymmetric monomers is a prerequisite for structural regularity. Furthermore, an important factor determining structural regularity is the relative concentration of these functional groups during the polycondensation. For bipolymers these relative concentrations can be controlled during synthesis, making control of structural regularity possible. For the case of bipolymers from one nonsymmetric monomer, only head-to-head/tail-to-tail regularity can be obtained.

1. Introduction

1.1. Systems Considered.

Linear polymers give rise to structural isomerism if some of their monomeric units can be distinguished in their relative orientation. A sufficient condition for a unit to be distinguishable in different orientations is the absence of twofold rotation axes, except if they are parallel to the "backbone". In the first paper of this series[1] these isomerism phenomena have been quantitatively investigated in some polyamides, both by quantitative chemical degradation and by NMR analysis of the polycondensates. Since the objective of our research is to control the isomerism during polycondensation, we have theoretically investigated the factors influencing structural isomerism during polycondensation. We consider polycondensation reactions of homobifunctional monomers and limit ourselves to the discussion of homo- and bipolycondensates.

In general, structural regularity is determined only to a very small extent by thermodynamic factors. In fact, two polymers consisting of macromolecules of equal chain length and having the regular structures I and II, for instance, can be expected to have somewhat different thermodynamic stability, but the difference is probably small. If polymer I or II is equilibrated with respect to the orientation of the ab units the structural regularity will, in general, be negligible, since the random orientation of



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*To whom correspondence should be addressed at the Massachusetts Institute of Technology.

0024-9297/84/2217-2248$01.50/0

nonsymmetric units contributes to the entropy of the system. Kinetic factors can determine structural regularity, however, to a very large extent, and we will consider only the case of kinetically controlled (irreversible) elementary reactions.

The theory as developed in this paper can also be applied to reactions where no low molecular mass material is eliminated, e.g., for the formation of polyurethanes from diisocyanates and diols.

A factor conceivably relevant for the determination of structural regularity is the kinetic reaction order with respect to individual functional groups. However, detailed consideration, not included in this report, reveals that the reaction order does not affect structure significantly except in the rare circumstance where the reaction order is higher than one *and* specific for one of several functional groups of the same type. For this case (and no example is known to the authors) it is easy to demonstrate that the maximum achievable structural regularity is always lower than for the simple cases with first-order reaction with respect to the individual functional groups. We therefore consider only systems with kinetics of first order with respect to the concentrations of the functional groups involved in the polycondensations.

A further factor relevant for structural isomerism, ceteris paribus, is the possible interdependence of the reactivity of the two functional groups (of the same type) in a monomer molecule, i.e., the change in the reactivity of a functional group with reaction of the other functional group in the same molecule. In this paper we will only consider monomers in which no such interdependence exists.

Although condensation polymers with some degree of structural regularity[2,3] have been prepared before this work was started,[4,5] the theoretical aspects of this type of polycondensation have not been systematically investigated. Kuchanov has published the theory of the "nonequilibrium" terpolymerization of symmetric monomers,[6,7] and the theory was extended by Korshak et al.[8] to obtain the result for one limiting case of a system with structural isomerism.[9] We intend to develop a fuller description of the factors determining structural regularity.

We will, in this paper, only consider homogeneous reaction phases, although the overall system might have more than one phase (e.g., one of the monomers might be brought into solution by dissolving from the crystalline form[8] or by diffusion from another, immiscible liquid phase).

In the following we will first define a parameter, s, that describes the nearest-neighbor statistics of orientation of nonsymmetric groups. Then we shall briefly consider the molecular mass distribution of these polycondensates (investigated already by other authors). Finally we shall investigate the cases of the homopolymers from one nonsymmetric monomer (XabX), of the bipolymers from one symmetric and one nonsymmetric monomer (XabX + YccY), and the bipolymers from two nonsymmetric monomers (XabX + XcdY).

1.2. Quantitative Description of Structural Regularity. The units whose orientation in the chain can be distinguished (e.g., the units from the XabX monomer) are called "nonsymmetric", and other units (e.g., the units from a YccY monomer) are called "symmetric". The degree of orientational order (i.e., of structural regularity) in the polymer can be quantified in different ways. We chose as descriptive parameter the probability of two adjacent nonsymmetric units to point in the same direction and call it s

$$s = \text{probability for two adjacent units to point in the same direction,} \quad 0 \leq s \leq 1 \quad (1)$$

For a chain where all units point in the same direction $s = 1$ ("head-to-tail" enchainment); when the orientation of the units is strictly alternating $s = 0$ ("head-to-head/tail-to-tail" enchainment). If no preference for the different enchainments exists $s = {}^1/_2$ ("random" chain). All polymers considered here are supposed to be statistically homogeneous, and the question of block polymers is not investigated since we limit ourselves to one-step polycondensation. It is important, however, to point out that the parameter s, even with this limitation, is not sufficient to describe the structural isomerism in all polycondensates considered. For regular polymers with only one type of nonsymmetric monomer the value of s sufficiently describes the degree of structural regularity, but if more than one type of nonsymmetric monomer is present new parameters are required. For instance, for the bipolymer from two nonsymmetric monomers, the case XabX + YcdY considered later on in this paper, two additional parameters are needed to take account of orientational correlations between units of the same type, i.e., next-to-the-nearest-neighbor statistics.

Kuchanov's "degree of microheterogeneity" K_m[6,7] which is equal to Yamadera and Murano's "degree of randomness" B[10,11] for the systems considered here, is applicable to the cases of homopolymer and bipolymer with one nonsymmetric unit. The relationship between K_m (or B) and s depends on the extent of reaction and on the system under consideration. For complete reaction, where $1/\bar{x}_n \rightarrow 0$, the value for K_m is simply double that for s

$$K_m \equiv B = 2s, \qquad 100\% \text{ conversion } (1/\bar{x}_n \rightarrow 0) \quad (2)$$

1.3. Molecular Mass Distribution. The chain length distribution of simple condensation polymers conforms to the "most probable" distribution if the principle of chain length independent reactivity is assumed. This is true for polymers formed irreversibly as well as under conditions of equilibrium.[12-14] Case[15] has elaborated the system XabX + YccY in detail. His results show that the six different polymer species formed if only end groups are considered and structural isomerism is neglected, namely, Xa--aX, Xa--bX, Xa--cY, Xb--bX, Xb--cY, and Yc--cY, all obey individually distribution laws corresponding to the "most probable" distribution. One can think of the system as having, on the average, the "most probable" distribution with oscillations around the mean curve.[16] This holds true even in much more complicated systems with many comonomers.[17-19] Adherence to a distribution of this type is tacitly assumed in the rest of this paper. Equimolarity of the reacted functional groups at the end of the reaction is necessary in all systems in order to obtain high average molecular masses, and we will consider only this case.

In addition to these considerations there is, of course, the fact that loss of material (particularly of oligomers) usually alters the molecular mass distribution, and the possibility exists that loss of material is structurally selective, since the regular polymers are often much less soluble in the usual solvents than the irregular ones.[5,20,21] For these reasons only the degree of regularity obtained on polymer samples containing essentially all chains formed during synthesis (including oligomers) can be compared with the values obtained from theory as developed in this report.

Polycondensation invariably leads to cyclic compounds, and ring formation influences the molecular mass distribution.[22] However, the influence of ring formation on

Table I
Simplifying Assumptions Used in This Work

one-step synthesis
irreversible (kinetically controlled) condensation reactions
not more than two different monomers
first-order reactions with respect to the concentrations of the functional groups involved in polycondensation
independence of the reactivity of the two functional groups in a monomer molecule
chain length independence of reactivity
homogeneous reaction phases
on the average "most probable" molecular mass distribution for high extents of reaction
equimolarity of reacted functional groups at the end of the polycondensations
rings can be ignored

structural regularity is not expected to be substantial, and ring formation is therefore ignored in this paper.

The simplifying assumptions made in this theoretical approach are summarized in Table I and will be applied without further mention in the rest of this paper.

2. Homopolymers: The System XabX

2.1. Elementary Reactions. The simplest possible polycondensation system is the one where a single nonsymmetric monomer, XabX, reacts (–aX with –aX or –bX, and –bX with –bX; X is a leaving group only) to form chains with –ab– units. Polyanhydrides may represent an example of this type. In the simplest analysis four elementary condensation steps are involved

$$-\mathrm{aX} + \mathrm{Xa}- \xrightarrow{r_a} -\mathrm{a|a}- + 2\mathrm{X} \tag{3a}$$

$$-\mathrm{aX} + \mathrm{Xb}- \xrightarrow{1} -\mathrm{a|b}- + 2\mathrm{X} \tag{3b}$$

$$-\mathrm{bX} + \mathrm{Xa}- \xrightarrow{1} -\mathrm{b|a}- + 2\mathrm{X} \tag{3c}$$

$$-\mathrm{bX} + \mathrm{Xb}- \xrightarrow{r_b} -\mathrm{b|b}- + 2\mathrm{X} \tag{3d}$$

where all rate constants were divided by the one of the second or third reaction (k_{ab}), $r_a = k_{aa}/k_{ab}$ and $r_b = k_{bb}/k_{ab}$, for convenience, and the vertical bars between a's and b's were employed to avoid ambiguous use of the term "ab". Usually one will not be able to distinguish between the second and the third reaction. The probability s is given here by

$$s = [\mathrm{a|b}]/([\mathrm{a|a}] + [\mathrm{a|b}] + [\mathrm{b|b}]) \tag{4}$$

where [a|b] includes also the concentration of –b|a–.[23]

If $r_a = r_b = 1$, i.e., if all reaction rate constants in (3a–d) are equal, the resulting polymer displays no structural order at all and $s = {}^1/_2$. If the reactivity ratios are larger or smaller than 1, however, structurally regular polymers can be obtained. An analysis of the kinetic equations governing the system will yield the principal possibilities.

2.2. Kinetics for the Homopolymer System. Considering a reaction phase where all of the monomer is present at the start of the reaction, we introduce relative concentrations for convenience

$$(\mathrm{A}) = [-\mathrm{aX}]/[-\mathrm{aX}]_0 \tag{5a}$$

$$(\mathrm{B}) = [-\mathrm{bX}]/[-\mathrm{aX}]_0 \tag{5b}$$

$$(\mathrm{AA}) = [\mathrm{a|a}]/[-\mathrm{aX}]_0 \tag{5c}$$

$$(\mathrm{AB}) = [\mathrm{a|b}]/[-\mathrm{aX}]_0 \tag{5d}$$

$$(\mathrm{BB}) = [\mathrm{b|b}]/[-\mathrm{aX}]_0 \tag{5e}$$

The number-average degree of polymerization is

$$\bar{x}_n = 2/[(\mathrm{A}) + (\mathrm{B})] \tag{6}$$

Table II
Values of s for Special Values of r_a and r_b for the Homopolymer from a Monomer XabX ($1/\bar{x}_n = 0$)

	$r_b = 0$	$r_b = 1$	$r_b \to \infty$
$r_a = 0$	1	0.632^a	0
$r_a = 1$	0.632^a	$^1/_2$	0
$r_a \to \infty$	0	0	0
		s	

[a] This value corresponds to $1 - 1/e$.

We are able to write the kinetic equations of the system in simple form, if we introduce a new parameter, θ

$$\theta = [-\mathrm{aX}]_0 k_{ab} t \tag{7}$$

(i.e., multiply the time t with a constant factor), where k_{ab} is the absolute rate constant of the reactions in eq 3b,c, and obtain a system of simultaneous nonlinear ordinary homogeneous first-order differential equations of the first degree

$$\mathrm{d(A)}/\mathrm{d}\theta = -2r_a(\mathrm{A})^2 - 2(\mathrm{A})(\mathrm{B}) \tag{8a}$$

$$\mathrm{d(B)}/\mathrm{d}\theta = -2(\mathrm{A})(\mathrm{B}) - 2r_b(\mathrm{B})^2 \tag{8b}$$

$$\mathrm{d(AA)}/\mathrm{d}\theta = r_a(\mathrm{A})^2 \tag{8c}$$

$$\mathrm{d(AB)}/\mathrm{d}\theta = 2(\mathrm{A})(\mathrm{B}) \tag{8d}$$

$$\mathrm{d(BB)}/\mathrm{d}\theta = r_b(\mathrm{B})^2 \tag{8e}$$

For special values of r_a and r_b simple algebraic solutions for this system of equations can be found. In general, however, one must use numerical integration.

In the special case where $r_a = r_b = r$, for instance, one obtains a perfect "head-to-tail" polymer (ab|) with $s = 1$ when $r = 0$, and a perfect "head-to-head/tail-to-tail" polymer (ba|ab|) with $s = 0$ when $r \to \infty$. It is easy to show that for any r the probability s is independent of the extent of reaction, and

$$s = 1/(1 + r), \qquad r_a = r_b = r \tag{9}$$

If $r = 1$ a "random" polymer with $s = {}^1/_2$ is obtained. Note that r must be very different from 1 for substantial regularities to be obtained.

If r_a and r_b are not equal, but one of both approaches infinity, s is also zero (since a symmetric dimer, XabbaX or XbaabX, is formed immediately). If one of both, r_a or r_b, is nearly zero and the other one is equal to unity the special situation arises where the first or last of the reaction equations in (3a–d) is eliminated. Here solution of the equations (8a–e) gives $s = 1 - 1/e = 0.63212...$ for complete reaction.

The results for special values of r_a and r_b are collected in Table II. Control over the structural regularity is only possible through changes in the reaction rate constants of the reactions in eq 3a–d.

3. Bipolymers: The System XabX + YccY

3.1. Principal Considerations. If a nonsymmetric monomer, XabX, is reacted with a symmetric monomer, YccY, so that the only reactions allowed are –cY with –aX or –bX to form –ac– and –bc– linkages and a product XY, polymer chains are obtained that contain alternatingly –ab– and –cc– groups. The shortest structural elements affected by the mutual orientation of –ab– units in the chains are

$$-\mathrm{acca}- \qquad -\mathrm{accb}- \qquad -\mathrm{bcca}- \qquad -\mathrm{bccb}- \tag{10}$$

where the two structures in the middle will be indistinguishable, in general. The first and the last arrangements indicate that two adjacent –ab– units point in different directions; in the other two arrangements the units are oriented the same way. The probability s is given here by

$$s = [\text{accb}]/([\text{acca}] + [\text{accb}] + [\text{bccb}]) \qquad (11)$$

and [accb] includes –accb– as well as –bcca– arrangements. A relevant parameter determining the degree of regularity is the ratio, r, of the reaction rate constants for the reaction –aX + Yc– → –ac– and for the reaction –bX– + Yc– → –bc–

$$r = k_{\text{bc}}/k_{\text{ac}}, \qquad 0 \leq r \leq 1 \qquad (12)$$

where we have arbitrarily chosen –aX to be the faster reacting group.

The relevant elementary reactions and their relative rate constants, divided by the absolute rate constant of the first reaction, k_{ac}, are

$$\text{YccY} + \text{Xa–} \xrightarrow{1} \text{–accY} + \text{XY} \qquad (13\text{a})$$

$$\text{YccY} + \text{Xb–} \xrightarrow{r} \text{–bccY} + \text{XY} \qquad (13\text{b})$$

$$\text{–accY} + \text{Xa–} \xrightarrow{1} \text{–acca–} + \text{XY} \qquad (13\text{c})$$

$$\text{–accY} + \text{Xb–} \xrightarrow{r} \text{–accb–} + \text{XY} \qquad (13\text{d})$$

$$\text{–bccY} + \text{Xa–} \xrightarrow{1} \text{–bcca–} + \text{XY} \qquad (13\text{e})$$

$$\text{–bccY} + \text{Xb–} \xrightarrow{r} \text{–bccb–} + \text{XY} \qquad (13\text{f})$$

If the two identical functional groups in the nonsymmetric monomer are equally reactive ($r = 1$) the mutual orientation of the ab units in the polymer will be random and $s = {}^1/_2$. If $r < 1$, however, different structural order is obtained, as Preston[3] has realized first, depending on the method used in the polycondensation. The factor operative here is the relative concentration of –aX and –bX groups, which can be controlled during the synthesis. This shall be illustrated with the simple case where $r \rightarrow 0$ and the reaction is complete (i.e., the case where the two functional groups in the nonsymmetric monomer are very different in reactivity and all monomers are joined to form a single chain):

If all of the two monomers are mixed at once (before the first condensation step occurs), after a given time all –aX will have reacted, but no –bX yet. The species present then are XbaccabX, XbaccY, and YccY, in the proportion 1/4:1/2:1/4, since the probability of a –cY having reacted is ${}^1/_2$ and the probability of a –cY not having reacted is also ${}^1/_2$. Further reaction will join all remaining functional groups to yield a polymer with –acca–, –accb–, and –bccb– arrangements in the same proportions, and $s = {}^1/_2$. Thus, immediate mixing of all the reactants gives a random polymer.

If we add YccY slowly to all of XabX so that there will never be any unreacted –cY groups, the only species present after half of the YccY is added to the mixture will be XbaccabX. Upon addition of the rest of YccY, further condensation will yield –bccb– structures only, the resulting high polymer will contain –acca– and –bccb– arrangements only, and $s = 0$. Slow addition of YccY gives a "head-to-head/tail-to-tail" polymer.

If we finally add XabX slowly to YccY, we can follow two different paths: (i) We add XabX just so slowly that all –aX groups are always reacted but –bX groups have not reacted yet; after all XabX has been added we then have again the species XbaccabX, XbaccY, and YccY in the proportions 1/4:1/2:1/4, and further reaction yields a polymer with $s = {}^1/_2$. (ii) We add XabX so slowly that both –aX and –bX groups have always reacted, and the process will go on exactly as if $r = 1$; hence $s = {}^1/_2$ again. Addition of XabX to YccY gives a random polymer.

Polycondensates with ${}^1/_2 < s \leq 1$ cannot be obtained with simple procedural variations, since we exhausted all procedural possibilities for one-step synthesis. However, if the reactivity of the –cY groups in YccY is not independent from each other, this possibility exists; we shall pursue this in a future paper.

3.2. Kinetics for the System XabX + YccY.

The kinetics of the system XabX + YccY have already been investigated by other researchers: Ozizmir and Odian[24] found the time-dependence of the concentrations of functional groups as well as of $\bar{x}_{\text{n}}$. Gandhi and Babu[19] published similar work and included an investigation of the effect of interdependence between the two –cY groups in YccY. They also obtained expressions for $\bar{M}_{\text{w}}/\bar{M}_{\text{n}}$, but problems connected with structural regularity were ignored.

The appropriate system of reactions is given by eq 13a–f. As convenient variables we use relative concentrations

$$(\text{A}) = [\text{–aX}]/[\text{a}]_{\text{sto}} \qquad (14\text{a})$$

$$(\text{B}) = [\text{–bX}]/[\text{b}]_{\text{sto}} \qquad (14\text{b})$$

$$(\text{C}) = [\text{–cY}]/[\text{c}]_{\text{sto}} \qquad (14\text{c})$$

where the subscript "sto" stands for "stoichiometric". In cases where all a groups are present at the beginning of the reaction, $[\text{a}]_{\text{sto}} = [\text{–aX}]_0$. If XabX is added during the process, $[\text{a}]_{\text{sto}}$ is the amount of substance of the –a– group that will be present at the end of the addition (when equimolarity has been reached) per unit volume. The definition of $[\text{b}]_{\text{sto}}$ and $[\text{c}]_{\text{sto}}$ is completely analogous. Note that $[\text{c}]_{\text{sto}} = 2[\text{a}]_{\text{sto}} = 2[\text{b}]_{\text{sto}}$, since equimolarity of functional groups requires that $[\text{c}]_{\text{sto}} = [\text{a}]_{\text{sto}} + [\text{b}]_{\text{sto}}$. The relative concentrations of the other components in eq 13a–f are defined by

$$(\text{CC}) = [\text{YccY}]/[\text{a}]_{\text{sto}} \qquad (15\text{a})$$

$$(\text{ACC}) = [\text{–accY}]/[\text{a}]_{\text{sto}} \qquad (15\text{b})$$

$$(\text{BCC}) = [\text{–bccY}]/[\text{a}]_{\text{sto}} \qquad (15\text{c})$$

$$(\text{ACCA}) = [\text{–acca–}]/[\text{a}]_{\text{sto}} \qquad (15\text{d})$$

$$(\text{ACCB}) = [\text{–accb–}]/[\text{a}]_{\text{sto}} \qquad (15\text{e})$$

$$(\text{BCCB}) = [\text{–bccb–}]/[\text{a}]_{\text{sto}} \qquad (15\text{f})$$

Material balance yields (C) = (CC) + [(ACC) + (BCC)]/2 immediately.

The kinetic equations for the system of reactions displayed in eq 13a–f become particularly manageable if we scale time according to (see also eq 7)

$$\theta = [\text{a}]_{\text{sto}} k_{\text{ac}} t \qquad (16)$$

where k_{ac} is the absolute rate constant for the first reaction in the system (13a–f), and define two "feed functions" that describe how much of XabX or YccY is added at a given "time" θ

$$\text{d}Y(\theta) = \text{d}[\text{XabX}]_{\text{added}}/[\text{a}]_{\text{sto}}$$

$$\text{d}Z(\theta) = \text{d}[\text{YccY}]_{\text{added}}/[\text{a}]_{\text{sto}} \qquad (17)$$

The integrated functions Y and Z are the fractions of the two monomers already added. The resulting kinetic equations form a system of simultaneous nonlinear ordinary inhomogeneous first-order differential equations of the first degree:

$$d(A)/d\theta = 2(A)(CC) - (A)(ACC) - (A)(BCC) + dY/d\theta \tag{18a}$$

$$d(B)/d\theta = -2r(B)(CC) - r(B)(ACC) - r(B)(BCC) + dY/d\theta \tag{18b}$$

$$d(CC)/d\theta = -2(A)(CC) - 2r(B)(CC) + dZ/d\theta \tag{18c}$$

$$d(ACC)/d\theta = +2(A)(CC) - (A)(ACC) - r(B)(ACC) \tag{18d}$$

$$d(BCC)/d\theta = +2r(B)(CC) - (A)(BCC) - r(B)(BCC) \tag{18e}$$

$$d(ACCA)/d\theta = +(A)(ACC) \tag{18f}$$

$$d(ACCB)/d\theta = +r(B)(ACC) + (A)(BCC) \tag{18g}$$

$$d(BCCB)/d\theta = +r(B)(BCC) \tag{18h}$$

that becomes homogeneous when $dY(\theta) = dZ(\theta) = 0$, when all of both monomers is mixed before the beginning of the polycondensation. The system of equations (18a–h) can be integrated numerically; it becomes stiff as r approaches zero, and in the numerical solutions Gear's method[25] was used.

In order to check the integration an independent numerical solution was obtained in some instances by a Monte Carlo technique. The reaction was simulated, starting, to take as an example a case where everything is mixed at the beginning, with 100'000 XabX monomers and an equal number of YccY monomers. A reaction step is performed as follows:

(i) A random number from a uniform distribution is chosen (a mixed-congruential random number generator was employed[26] and used to decide whether an –aX or a –bX group would react according to r and the relative numbers of –aX and –bX groups.

(ii) A second random number is chosen to pick a specific group from the chosen type (–aX or –bX).

(iii) A third random number is taken to select a specific –cY group.

(iv) The "reaction" is carried out by subtracting 1 from the counters that keep track of the chains where the –aX (or –bX) groups and the –cY groups come from and by adding 1 to the counter that keeps track of the newly formed species, and, if necessary, by incrementing the counter for the –acca–, –accb–, or –bccb– arrangements. This cycle of four steps is repeated until the desired extent of reaction is reached. For $\bar{x}_n > 2$ the results obtained in this fashion agree with those obtained by numerical integration to within 0.02; this is the estimated 2σ confidence limit of the Monte Carlo average. At lower extents of reaction, too few arrangements are formed to warrant definitive conclusions.

Before pursuing the solution of the system of differential equations (18a–h) in the following sections, we will inspect some relationships of interest to all cases.

The number-average degree of polymerization is always equal to the number of monomeric units in the system divided by half the number of chain ends. If N_{sto} denotes the total number of monomeric units in the system at the end of the polycondensation, the number of monomeric units at "time" θ is given by

$$N(\theta) = N_{sto}\int_0^\theta [dY(x) + dZ(x)]\, dx = Y + Z \tag{19}$$

and the number of chain ends, M, is given by

$$M(\theta) = N_{sto}[(A) + (B) + 2(C)] \tag{20}$$

The number-average degree of polymerization therefore is

$$\bar{x}_n = 2(Y + Z)/[(A) + (B) + 2(C)] \tag{21}$$

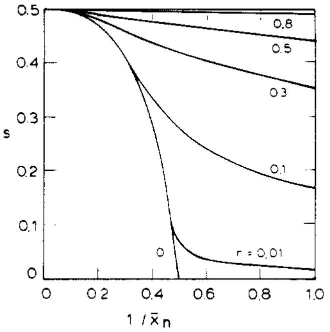

Figure 1. Structural order as a function of the degree of polymerization when all of XabX and YccY is mixed before the beginning of polycondensation, using eq 27 and 28.

Another quantity of interest is the difference between [acca] and [bccb], since for chains of finite length these two quantities usually are not equal. Defining Δ to be the difference between (ACCA) and (BCCB) we obtain by a balance of the unreacted groups –aX and –bX the result

$$\begin{aligned}\Delta &= ([acca] - [bccb])/([acca] + [accb] + [bccb]) \\ &= [(B) - (A)]/[2 - (A) - (B)]\end{aligned} \tag{22}$$

The "coefficient of microheterogeneity" defined by Kuchanov[6,7] is given for this case and in our notation as

$$K_m = \frac{(ACCB)}{(ACCB) + 2(ACCA)} + \frac{(ACCB)}{(ACCB) + 2(BCCB)} \tag{23}$$

and is identical with B as defined by Yamadera and Murano[10,11] when applied here. The relationship between K_m, or B, and s is

$$K_m \equiv B = 2s/(1 - \Delta^2) \tag{24}$$

which simplifies, for complete reaction, to eq 2. For not too high extent of reaction K_m is somewhat larger than $2s$; this can give the false impression of some order of the type $s > {}^1/_2$.

3.3. Cases Where All of XabX Is Present at the Start of the Reaction.

If all of XabX is present at the beginning of the reaction $dY(\theta) = 0$ for all $\theta > 0$, and

$$(B) = (A)^r$$

$$d(B) = r(A)^{r-1}\, d(A) \tag{25}$$

Immediately eq 22 gives

$$\Delta = [(A)^r - (A)]/[2 - (A) - (A)^r] \tag{26}$$

3.3.1. "All at Once".

If all of the YccY is also present at the beginning of the reaction, the resulting chains display essentially random orientation for 100% conversion (see above). For incomplete reaction a simple approximation is derived from the probability for an –aX group having reacted, $1 - (A)$, and that for a –bX group having reacted, $1 - (B)$. Since $(ACCA) \approx [1 - (A)]^2$, $(ACCB) \approx 2[1 - (A)][1 - (B)]$, and $(BCCB) \approx [1 - (B)]^2$, we obtain

$$s \approx 2[1 - (A)][1 - (A)^r]/[2 - (A) - (A)^r] \tag{27}$$

The effect of chain ends carrying –cY groups is neglected here, since an error of similar magnitude and equal sign occurs in the numerator and the denominator, and since this error vanishes with increasing chain length. With eq 21 and the fact that material balance requires $2(C) = (A) + (B)$ we get

$$\bar{x}_n = 2/[(A) + (A)^r] \tag{28}$$

Numerical integration of the homogeneous system of equations (18a–h) ($dY = dZ = 0$) yielded values in excellent agreement with those of eq 27. In Figure 1 we plot s after eq 27 against $1/\bar{x}_n$ after eq 28 for different values of r. One sees that for all cases of practical interest, i.e., when $\bar{x}_n > 10$, $0.48 < s < 0.5$. The relative difference between the two symmetric arrangements, Δ according to eq 22, can readily be calculated. Using the degree of polymerization from eq 28, one can state that

$$\Delta \leq 1/(\bar{x}_n - 1) \qquad (29)$$

3.3.2. "Infinitely" Slow Addition of YccY. If YccY is added to the reaction mixture during the polycondensation $dZ(\theta)$ is not zero and must be specified. A particularly simple possibility is "infinitely" slow addition, i.e., so slowly that there will never be more than infinitesimal amounts of chains with –cY ends. The relevant relative group concentrations will be (A), (B), (ACCA), (ACCB), and (BCCB). After a small amount of YccY is added, dZ, it will react completely and

$$d(A) + d(B) = -2(dZ) \qquad (30)$$

The relative probability of an –ac– bond being newly formed is $p = (A)/[(A) + r(B)]$, and one of a –bc– bond being formed is $1 - p$. The increments in the different arrangements from eq 10 are

$$d(ACCA) = p^2\, dZ \qquad (31a)$$

$$d(ACCB) = 2p(1 - p)\, dZ \qquad (31b)$$

$$d(BCCB) = (1 - p)^2\, dZ \qquad (31c)$$

and since $d(A)/d(B)$ must equal $p/(1 - p)$ we can obtain eq 31a–c in d(A) with the aid of eq 30

$$d(ACCA) = -d(A)/[2(1 + r(A)^{r-1})] \qquad (32a)$$

$$d(ACCB) = -r\, d(A)/(r + (A)^{1-r}) \qquad (32b)$$

$$d(BCCB) = -r^2\, d(A)/[2(A)^{1-r}(r + (A)^{1-r})] \qquad (32c)$$

The *instantaneous* probability for two adjacent –ab– units to point in the same direction, δs (the value of s in the infinitesimal amount of new arrangements just formed), is now

$$\delta s = 2r(A)^{1+r}/[(A) + r(A)^r]^2 \qquad (33)$$

While integration of the equations (32a–c) from the start of the reaction ((A) = 1) to the present value of (A) yields

$$s = \frac{2r}{2 - (A) - (A)^r} \int_{(A)}^{1} (r + x^{1-r})^{-1}\, dx \qquad (34)$$

The integral cannot be solved in closed form, but numerical values are readily computed. At the completion of the condensation, eq 34 takes on a particularly simple form[5,27]

$$s = r \int_0^1 (r + x^{1-r})^{-1}\, dx, \qquad 1/\bar{x}_n = 0 \qquad (35)$$

This equation is a reformulation of the one quoted without deduction by Korshak et al.[8]

The number-average degree of polymerization corresponding to a given value of (A) in eq 34 can be found by using eq 21 with $Y = 1$, $(C) = 0$, and $Z = 1 - [(A) + (B)]/2$,

$$\bar{x}_n = 4/[(A) + (A)^r] - 1 \qquad (36)$$

The relative difference between the two symmetric arrangements is for the case of "infinitely" slow addition given by

$$\Delta \leq 2/(\bar{x}_n - 1) \qquad (37)$$

Values for s vs. $1/\bar{x}_n$ for different values of r are plotted in Figure 2. The integral in eq 34 was evaluated to four significant digits using Simpson's rule. Also included in the graph is a dashed curve showing the instantaneous degree of order, δs, for $r = 0.1$. Focusing on the two curves for $r = 0.1$, those for s and δs, we observe that at the beginning of the reaction, when $1/\bar{x}_n = 1$, $s = \delta s = 2r/(1 + r)$. As the reaction proceeds the more reactive –aX groups are depleted faster than the –bX groups, and –bX groups react relatively more often. This leads to a decrease in orientational order, and hence to an increase in δs. s follows δs "sluggishly" since it is an averaged quantity. At a certain point most –aX groups will have reacted, and further reaction will involve –bX almost exclusively. Newly added YccY will form mostly –bccb– arrangements and δs drops rapidly. s follows slowly until $1/\bar{x}_n = 0$, but never reaches the initial low value. For $r < 0.5$ the maximum in s (as the reaction proceeds to completion) occurs at $1/\bar{x}_n > 0.1$; i.e., $\bar{x}_n < 10$. Hence, for cases of practical significance the higher $\bar{x}_n$, the higher the structural order.

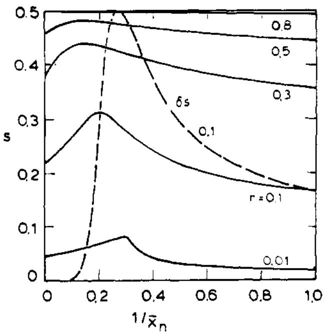

Figure 2. Structural order as a function of the degree of polymerization when YccY is added "infinitely slowly" to the reaction mixture containing XabX and products, using eq 34 and 36.

Equations 34 and 35 are not very convenient, but an approximation to eq 35 to better than 2% for $r < 0.1$ is

$$s \approx 1 - r^{r/(1-r)}, \qquad 1/\bar{x}_n = 0 \qquad (38)$$

3.3.3. Adding YccY at a Finite Rate. The "infinitely" slow addition allows for algebraic solutions; they indicate clearly that small values of s can be obtained. Since mixing "all at once" before the start of the reaction produces essentially random structures, the rate of addition must be an independent variable that controls the degree of regularity. But if YccY is added faster than at an infinitesimal rate, the feed function $dZ(\theta)$ must be specified for the system of kinetic equations (18a–h) to be soluble.

As an example we will consider the case where the symmetric compound YccY is fed to the reaction mixture in such a way that the relative concentration of –cY groups, (C), is constant at a preset level, q, until the amount of YccY required for equimolarity is reached ($Z = 1$). After that the reaction will proceed to completion without further addition. Infinitely slow addition corresponds to a value of $q = 0$, while $q = 1$ means that all of YccY and XabX is mixed before the reaction starts, and $0 \leq q \leq 1$, in any case. Probabilities s for this system were calculated by integration of eq 18a–h. Results, plotted vs. q for different values of r and $\bar{x}_n = 40$, are displayed in Figure 3. The effect of chain length is demonstrated for $r = 0.1$, where the curve for $\bar{x}_n = 15$ is drawn also, as a dashed line. It is evident that for given r the structural regularity in the polymer can be continuously varied between the highest possible regularity and complete "randomness" by varying q. The influence of the extent of reaction is far less dominant.

The requirement for constant C calls for special experimental conditions. If r is small we need only consider the reaction of –cY with –aX. The condition that

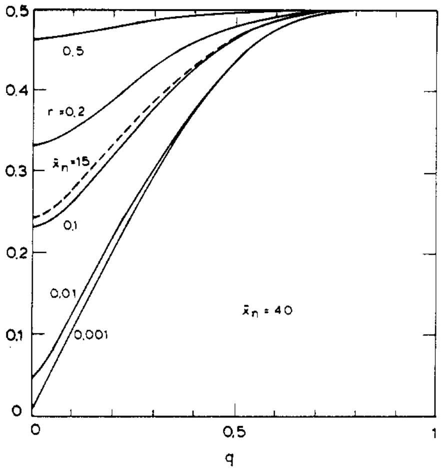

Figure 3. Structural order as a function of the rate of addition of YccY to the reaction mixture containing XabX and products, characterized by the relative concentration of –cY groups in the reaction mixture, (C), when (C) is held constant at a level q until the required amount of YccY is added.

$\mathrm{d}[-\mathrm{cY}]/\mathrm{d}t = 0$ yields then the required concentration increment per unit time

$$\mathrm{d}[\mathrm{YccY}]_{\mathrm{added}}/\mathrm{d}t \approx qk_{\mathrm{ac}}[-\mathrm{aX}]_0^2 \exp(-qk_{\mathrm{ac}}[-\mathrm{aX}]_0 t) \qquad (39)$$

with the dimension mol/(L·s), for instance. Here, k_{ac} is the absolute rate constant of the reaction in eq 13a. If r is not very small an expression replacing eq 39 can be obtained from the known exact solutions of the kinetic equations, determined by Ozizmir and Odian[24] and Gandhi and Babu.[19]

These calculations can be performed to conform to any conceivable method of addition, e.g., at constant rate, stepwise, etc., and the principal shape of s vs. q for those conditions can be computed. Complete control over the structural regularity is always possible.

3.4. Adding XabX to YccY. In an earlier section of this report the conclusion has been reached that for high extent of reaction only values of $s = {}^1/_2$ could be achieved if XabX is added to YccY. Numerical integration of 18a–h with dZ = 0 showed that when XabX is added to the reaction mixture the probability s approaches the random value of ${}^1/_2$ even faster than when all of XabX and YccY is mixed at once (compare also Figure 1). This is true for all r, and in the limit of "infinitely" slow addition of XabX to the mixture $s = {}^1/_2$ from the start of the reaction.

4. Bipolymers: The System XabX + YcdY

If two nonsymmetric monomers, XabX and YcdY, react so that –aX or –bX condensate with –cY or –dY only, the resulting chains contain –ab– and –cd– groups alternatingly. Here, the shortest structural segment affected by orientation of units is a diad, and the orientational arrangements can be described by the frequency of linkages –ac–, –ad–, –bc–, and –bd–. We define s by

$$s = ([\mathrm{bc}] + [\mathrm{ad}])/([\mathrm{ac}] + [\mathrm{ad}] + [\mathrm{bc}] + [\mathrm{bd}]) \qquad (40)$$

This single parameter is not, however, sufficient to describe the possible structures obtainable by a simple one-step synthesis. For the case of the bipolymer with one nonsymmetric monomer, discussed above, we have found that a correlation between "adjacent" ab groups is easily achieved *over* a symmetric unit. Since the present case, XabX + YcdY, degenerates to the case discussed above when –cY and –dY are equally reactive, a correlation between ab units must also here be taken into consideration. The same is true for the cd units.

Table III
Special and Limiting Cases for the System XabX + YcdY (xx is either ab or ba; yy is either cd or dc)

	s_1	s_2	s	structure
regular polymers				
1	1	1	1	(abcd)
2	1	1	0	(abdc)
3a	1	0	${}^1/_2$	(abcdabdc)
3b	0	1	${}^1/_2$	(abcdbacd)
4	0	0	${}^1/_2$	(abcdbadc)
semiregular polymers				
5a	1	${}^1/_2$	${}^1/_2$	(abyy)
5b	${}^1/_2$	1	${}^1/_2$	(xxcd)
6a	0	${}^1/_2$	${}^1/_2$	(abyybayy)
6b	${}^1/_2$	0	${}^1/_2$	(xxcdxxdc)
irregular polymer				
7	${}^1/_2$	${}^1/_2$	${}^1/_2$	(xxyy)

In analogy to s we therefore define two additional parameters, one for the first monomeric unit, ab, and one for the second monomeric unit, cd (see also eq 11)

$$s_1 = \text{probability for two nearest ab units to point in the same direction}, \quad 0 \le s_1 \le 1$$
$$= ([\mathrm{acdb}] + [\mathrm{adcb}])/([\mathrm{acda}] + [\mathrm{acdb}] + [\mathrm{adcb}] + [\mathrm{bcdb}])$$
$$s_2 = \text{probability for two nearest cd units to point in the same direction}, \quad 0 \le s_2 \le 1$$
$$= ([\mathrm{cabd}] + [\mathrm{cbad}])/([\mathrm{cabc}] + [\mathrm{cabd}] + [\mathrm{cbad}] + [\mathrm{dabd}]) \qquad (41)$$

The "coefficient of microheterogeneity" is not applicable to this case.

The special and limiting cases in which all possible combinations of the values 0, ${}^1/_2$, or 1 are assigned to s_1, s_2, and s are listed in Table III. A full analysis of the reaction system is outside of the scope of this report, but it is interesting to note that regular, semiregular, and irregular polycondensates are possible as products of a one-step synthesis. The four relevant elementary reactions are

$$-\mathrm{aX} + \mathrm{Yc}- \xrightarrow{k_{\mathrm{ac}}} -\mathrm{ac}- + \mathrm{XY} \qquad (42\mathrm{a})$$

$$-\mathrm{aX} + \mathrm{Yd}- \xrightarrow{k_{\mathrm{ad}}} -\mathrm{ad}- + \mathrm{XY} \qquad (42\mathrm{b})$$

$$-\mathrm{bX} + \mathrm{Yc}- \xrightarrow{k_{\mathrm{bc}}} -\mathrm{bc}- + \mathrm{XY} \qquad (42\mathrm{c})$$

$$-\mathrm{bX} + \mathrm{Yd}- \xrightarrow{k_{\mathrm{bd}}} -\mathrm{bd}- + \mathrm{XY} \qquad (42\mathrm{d})$$

In the simplest analysis one can assume that the reaction rate constants are solely determined by the relative reactivities of the functional groups in the two monomers. Two ratios of rate constants are then sufficient to describe the system

$$r_1 = k_{\mathrm{bc}}/k_{\mathrm{ac}}, \qquad 0 \le r_1 \le 1 \qquad (43\mathrm{a})$$

$$r_2 = k_{\mathrm{ad}}/k_{\mathrm{ac}}, \qquad 0 \le r_2 \le 1 \qquad (43\mathrm{b})$$

(and $k_{\mathrm{bd}}/k_{\mathrm{ac}} = \{k_{\mathrm{bc}}/k_{\mathrm{ac}}\}\{k_{\mathrm{ad}}/k_{\mathrm{ac}}\} = r_1 r_2$) and the four reactions in eq 42 with their relative rate constants are

$$-\mathrm{aX} + \mathrm{Yc}- \xrightarrow{1} -\mathrm{ac}- + \mathrm{XY} \qquad (44\mathrm{a})$$

$$-\mathrm{aX} + \mathrm{Yd}- \xrightarrow{r_2} -\mathrm{ad}- + \mathrm{XY} \qquad (44\mathrm{b})$$

$$-\mathrm{bX} + \mathrm{Yc}- \xrightarrow{r_1} -\mathrm{bc}- + \mathrm{XY} \qquad (44\mathrm{c})$$

$$-\mathrm{bX} + \mathrm{Yd}- \xrightarrow{r_1 r_2} -\mathrm{bd}- + \mathrm{XY} \qquad (44\mathrm{d})$$

For limiting values of the reactivity ratios the following situations exist:

> If $r_1 = r_2 = 1$ only random polymers are produced (structure 7 in Table III).
>
> If only one ratio is equal to unity s must also equal $^1/_2$ and no nearest-neighbor correlation exist, but the system can exhibit next-to-the-nearest-neighbor regularity. If, for instance, $r_2 = 1$, the system corresponds effectively to the case XabX + YccY, discussed above, and an orientational correlation between –ab– units can be achieved by slowly adding YcdY to XabX (structure 6a in Table III if $r_1 = 0$ and $r_2 = 1$; structure 6b can be obtained if $r_1 = 1$ and $r_2 = 0$).
>
> Finally, if r_1 and r_2 are both smaller than unity, their magnitudes are crucial. If $r_1 = r_2 = 0$, the resulting polymer consists of repeat units of the type –bacd– only, and $s_1 = s_2 = 1$ and $s = 0$ (structure 2 in Table III). The same regularity is obtained here regardless of the synthetic procedure. As soon as r_1 and r_2 are larger than zero, however, procedural control over s exists again, similar to the situation in the system XabX + YccY, and different degrees of regularity can be achieved.

Evaluation of real systems will probably necessitate introduction of a new parameter, $r_{12} = k_{bd}/k_{ac}$, instead of the product r_1r_2. To date, no experiments on systems of the type XabX + YcdY have been reported.

5. Conclusions

According to the results obtained above, it appears that structural regularity in polycondensates, obtained from at least one nonsymmetric monomer in one synthetic step, can be significant and sometimes very high. In the homopolymer system considered the only factors determining this regularity are ratios of reaction rate constants, i.e., structural parameters; the proportions of the reacting groups cannot be varied. In the bipolymer systems considered (the systems XabX + YccY and XabX + YcdY), however, the relative concentrations of the functional groups on the nonsymmetric monomer(s) play an important role. This is in agreement with the fact that the structural regularity depends on the relative rate by which new bonds connecting the monomeric units are formed. The rates depend on the kinetic constants and the relative reactant concentrations, and in cases where the proportions of the functional groups can be influenced, both the reactivity of the functional groups and the relative concentrations must play a role. Through control of the relative concentrations of these functional groups one can always control structural regularity in the system XabX + YccY. In the system XabX + YcdY control can be achieved if both ratios of reaction rate constants are not too small.

The system investigated most thoroughly is the one with one nonsymmetric and one symmetric monomer, XabX + YccY. The factors most relevant to structural regularity here are the ratio of the reaction rate constants of groups –bX and –aX, the extent of reaction (i.e., the number-average degree of polymerization), and the relative concentration of –aX and –bX groups during the course of the polycondensation. Detailed quantitative relations were determined for special cases, and a general reaction scheme allows numerical solutions. The maximal achievable regularity depends on the ratio betweeen the reactivities of the two equal functional groups in the nonsymmetric monomer only and can be easily calculated. Regularity of the head-to-tail type cannot be achieved by using monomers in which the reactivity of the functional groups remain unchanged when one of the groups has reacted. Structural regularity of the head-to-head/tail-to-tail type can be controlled continuously between the maximum possible regularity and the random structure case simply by the rate of addition of one monomer to the other. This opens the way to the preparation of different polymers from the same monomers and with the same composition and thus to obtain polymers with predetermined and fine-tunable properties (e.g., softening temperature, solubility, water sorbtion, etc.) in the range given by the structurally completely irregular macromolecules and the polymer with known maximum achievable degree of regularity.

Acknowledgment. We thank the Schweizerischer Nationalfonds fuer die Foerderung der Wissenschaften for support under Grant No. 2.301-0.81/B. Partial support for U.W.S. was obtained through the Texaco-Mangelsdorf Associate Professorship at M.I.T.

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(23) K_m or $B^{6,7,10,11}$ can be defined here as

$$K_m \equiv B = \frac{[a|b]}{[a|b] + 2[a|a]} + \frac{[a|b]}{[a|b] + 2[b|b]}$$

(=2s for complete reaction).
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