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Constitutional Isomerism in Step-Growth Polymers: Theoretical Aspects of Systems with Chemical Induction

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ABSTRACT: A model was developed to determine the constitution of step-growth polymers synthesized from the nonsymmetric XabX monomer and the symmetric YccY monomer under various types of mixing modes. Depending upon the inherent kinetics of the system and the modes of addition of monomers, constitution (defined by the probability, s, that two adjacent nonsymmetric monomeric units in the polymer point in the same direction) can be varied over wide ranges. Results are shown for all variations of kinetic parameters and mixing modes. More detailed molecular level structure was determined by using a Monte Carlo technique.

Introduction

Constitutional isomerism in chemical compounds arises from differences in the nature or sequence of bonding. Linear polymer chains give rise to a constitutional isomerism if they contain "nonsymmetric" monomeric units such that arrangements with different mutual orientations can be distinguished (a sufficient condition for this is that the nonsymmetric units have no 2-fold rotation axes unless they are parallel to the polymer "backbone").

This isomerism has been well studied in chain-growth macromolecules (the terms "head-to-tail" and "head-to-head/tail-to-tail" are associated with it), but constitutional isomerism is generally not controllable nor does it play a great role in determining the properties of most of the resulting polymers.[1-3] The situation is quite different in step-growth polymers, which can also exhibit constitutional isomerism, and this phenomena has been used since the 1950s to explain unusual experimental results.[4-13] Suter and Pino[14] introduced an arbitrary but expedient classification into (i) polymers made from a single monomer (homopolymer), (ii) polymers made from two monomers (bipolymer), and (iii) polymers made from three or more monomers. They theoretically investigated the systems of homopolymer step-growth polymerization (of XabX) and the bipolymer step-growth polymerization of XabX and YccY. Their model assumed kinetically controlled (irreversible) single-step polymerization. Constitution of a polymer was determined to be affected by the reactivity differences of the functional groups of the nonsymmetric monomer and the manner in which monomers were mixed together. However, they limited their investigation to cases where functional groups react independently of each other, i.e., without chemical induction.

Here we used this model as a starting point and extended it to also describe systems where the reactivity of functional groups is dependent on the state of neighboring groups. We also incorporate greater flexibility in the manner in which monomers are added to the reaction mixture. Further, we investigated in detail the molecular structure of the polymer, e.g., the formation of "blocks". We focused on the system XabX + YccY, where the monomers can only react with each other, since extensive experimental data exists.[15-28] The methodology can, however, be used for other polymer systems as well.[29]

Among the questions addressed are (i) can the structure of a polymer be controlled in an easy and preselectable manner and (ii) does constitutional isomerism obtained in step-growth polymerization have a strong effect on the properties of the polymer? If both of these questions can be answered affirmatively, then control of structure would imply control over important properties. The ability to control constitutional isomerism in a single-stage synthetic scheme is the subject of this paper. It is, of course, possible to prepare polymers with highly ordered constitution in several synthetic steps; Takasuda et al.[30] have, for instance, prepared polymers with completely alternating orientation by sequential synthesis. Here, however, we focus not only on the regular extremes but also on the whole range of constitutional order.

Quantitative Description

When XabX is reacted with YccY such that the only reactions allowed are –cY + –aX → –ac– + XY and –cY + –bX → –bc– + XY (XY is a low molecular weight product that is not always produced), the polymer chains obtained contain alternately –ab– and –cc– groups. The shortest structural elements affected by the mutual orientation of –ab– units in the chains are

–acca– –accb– –bcca– –bccb–

Since in long chains –accb– arrangements are indistinguishable from –bcca– structures, the probability of two adjacent units pointing in the *same* direction, s, is given by

$$s = \frac{[\mathrm{accb}]}{[\mathrm{acca}] + [\mathrm{accb}] + [\mathrm{bccb}]} \tag{1}$$

where the brackets denote molar concentrations and [accb] includes both –accb– and –bcca– units.

The schematic shown in Figure 1 illustrates the first-order limiting cases of constitutional regularity in such a system (a triangle denotes an –ab– and a circle a –cc– unit). Polymers can be highly ordered in two modes: strictly alternating in a head-to-head/tail-to-tail arrangement ($s = 0$) or completely nonalternating in a head-to-tail arrangement ($s = 1$). Polymers that have a "perfectly random" constitution (polymers that are "completely disordered") will have an s value of 0.5 (the converse is not true, however; for example, polymers with very "blocky" structure can have a great deal of local order along the chain but still have a value of $s = 0.5$).

Systems Considered

Kinetic Control. Constitutional isomerism can, in principle, be determined by thermodynamic factors only.

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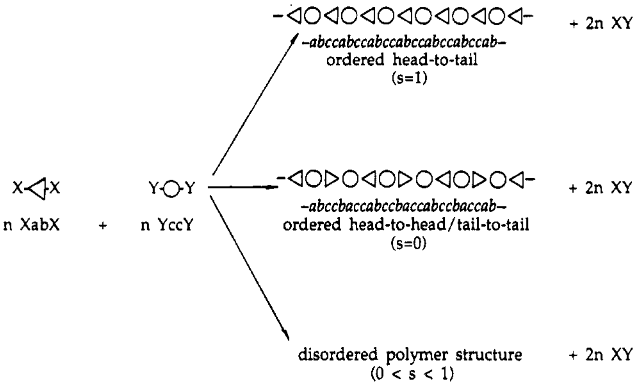

Figure 1. Schematic representation of sections of polymer structures of $\bar{x}_n = n$ with different order. X–◁–X indicates a nonsymmetric monomer, Y–○–Y indicates a symmetric monomer.

Table I
Simplifying Assumptions

one-stage synthesis (no side reactions)
irreversible (kinetically controlled) reactions
two different monomers
first-order reactions with respect to the concentrations of the functional groups involved in the polycondensation
chain-length independence of reactivity
homogeneous reaction phases
most probable distribution ($\bar{M}_w/\bar{M}_n \approx 2$) at high extent of reaction
equimolarity of reacted functional groups at the end of the polycondensation
rings can be ignored

In fact, two polymers consisting of equal chain length and having regular head-to-tail and head-to-head/tail-to-tail arrangements, respectively, can be expected to have somewhat different thermodynamic stability. Order of magnitude calculations show, however, that it is unlikely for s to fall outside the range $0.3 < s < 0.7$ through an equilibrium process.[31] Kinetic control is a prerequisite for high degrees of order.

What follows is the development of the kinetic model for the XabX + YccY polymerization system. As already stated, this development is an extension of an earlier one with the inclusion of greater detail in the choice of kinetic parameters that specify the system and more control over the type of feed mechanisms used. The molecular weight distribution is assumed, like in the earlier development, to conform to the "most probable" distribution. This and other simplifying assumptions in the theoretical development are listed in Table I.

Reaction Rate Parameters. The relevant kinetic parameters affecting constitutional isomerism are the relative reactivities of the functional groups in the nonsymmetric monomer and the mutual dependence of the reactivity of the functional groups in the symmetric monomer. The relative reactivities in the functional groups of the nonsymmetric monomer can arise from steric or electronic effects of the asymmetry. It is represented by r, the ratio of reaction rate constants for the reactions

$$-\mathrm{aX} + \mathrm{Yc}- \xrightarrow{-k_{\mathrm{aX}}} -\mathrm{ac}- + \mathrm{XY}$$

$$-\mathrm{bX} + \mathrm{Yc}- \xrightarrow{-k_{\mathrm{bX}}} -\mathrm{bc}- + \mathrm{XY}$$

so that

$$r = k_{\mathrm{bX}}/k_{\mathrm{aX}} \qquad 0 \le r \le 1 \tag{2}$$

where the –aX side of the monomer has been arbitrarily chosen to be the more reactive side.

The reactivity parameters g_a and g_b are the ratios of the reaction rate constants of the second reacting functional group on the YccY monomer to that of the first reacting functional group. The parameter g_a applies when the first reacting functional group of the YccY monomer has reacted with an –aX group, while g_b applies when the first one has reacted with a –bX. Thus, g_a compares the reactions $-\mathrm{X} + \mathrm{YccY} \rightarrow -\mathrm{ccY} + \mathrm{XY}$ and $-\mathrm{X} + \mathrm{Ycca}- \rightarrow -\mathrm{cca}- + \mathrm{XY}$. The comparison for g_b is analogous. Hence

$$g_a = k_{\mathrm{cY,second}}/k_{\mathrm{cY,first(-aX)}} \qquad 0 \le g_a \tag{3a}$$

$$g_b = k_{\mathrm{cY,second}}/k_{\mathrm{cY,first(-bX)}} \qquad 0 \le g_b \tag{3b}$$

These differences in the reactivities of –cY groups arise from electronic or steric effects, and the phenomenon is known as "induction". If there were no induction, $g_a = g_b = 1$. Deactivating induction means g_a (or g_b) < 1, while activating induction means g_a (or g_b) > 1. It is conceivable that induction also exists in the nonsymmetric monomer. However, the cases of interest involve $r \ll 1$ (and often less than 0.01). This, coupled with the fact that actual values for g_a and g_b are usually moderate in comparison and that the likely chemical structure of the nonsymmetric monomer is probably not conducive to strong chemical induction, causes this case not to be considered here.

One can write the relevant elementary reactions for this polymerization as follows. When the reactions are divided by the rate constant of the first reaction (k_{aX}), they become

$$-\mathrm{aX} + \mathrm{YccY} \xrightarrow{1} -\mathrm{accY} + \mathrm{XY} \tag{4a}$$

$$-\mathrm{bX} + \mathrm{YccY} \xrightarrow{r} -\mathrm{bccY} + \mathrm{XY} \tag{4b}$$

$$-\mathrm{accY} + -\mathrm{aX} \xrightarrow{g_a} -\mathrm{acca}- + \mathrm{XY} \tag{4c}$$

$$-\mathrm{accY} + -\mathrm{bX} \xrightarrow{rg_a} -\mathrm{accb}- + \mathrm{XY} \tag{4d}$$

$$-\mathrm{bccY} + -\mathrm{aX} \xrightarrow{g_b} -\mathrm{bcca}- + \mathrm{XY} \tag{4e}$$

$$-\mathrm{bccY} + -\mathrm{bX} \xrightarrow{rg_b} -\mathrm{bccb}- + \mathrm{XY} \tag{4f}$$

Modes of Addition of Monomers to the Reaction Mixture. Since high constitutional regularity can only be obtained through kinetic control, the most relevant parameters are the kinetic rate constants and the relative concentrations (i.e., feed rates) of the two monomers. One can distinguish three principal modes of mixing of the monomers: mode 1, XabX and YccY are mixed all at once (i.e., "infinitely fast mixing"); mode 2, XabX added to YccY; mode 3, YccY added to XabX. Analysis of modes 2 and 3 can be further refined by considering the rate of addition. Note that the mode 1 is the limit of fast addition for both modes 2 and 3; the extremes of "infinitely slow" mixing will be discussed separately for simplicity.

Kinetic Equations. To simplify the system of rate equations, the following convenient dimensionless variables are introduced

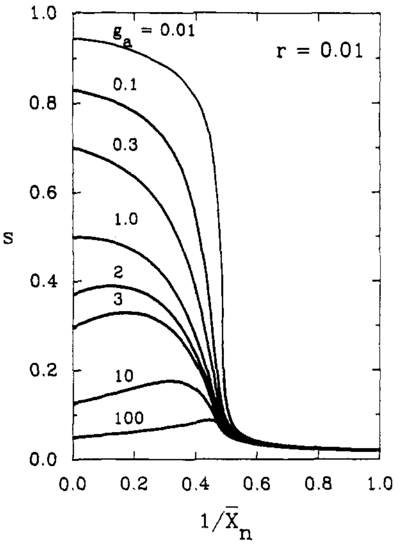

Figure 2. s as a function of the inverse degree of polymerization, $1/\bar{x}_n$ (showing extent of reaction), for various values of $g_a = g_b$. "All at once" mixing case.

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

$$(B) = [-bX]/[b]_{sto} \tag{5b}$$

$$(C) = [-cX]/[c]_{sto} \tag{5c}$$

where the subscript "sto" stands for stoichiometric. In cases where all the a groups are present at the beginning of the reaction, $[a]_{sto} = [-aX]_0$. If XabX is added during the course of the reaction, then $[a]_{sto} = [-a-]$ present at the end of the addition (at equimolarity). Similarly with $[b]_{sto}$ and $[c]_{sto}$. Note that $[c]_{sto} = 2[a]_{sto} = 2[b]_{sto}$. The relative concentrations of the other components can be defined by

$$(CC) = [YccY]/[a]_{sto} \tag{6a}$$

$$(ACC) = [-accY]/[a]_{sto} \tag{6b}$$

$$(BCC) = [-bccY]/[a]_{sto} \tag{6c}$$

$$(ACCA) = [-acca-]/[a]_{sto} \tag{6d}$$

$$(ACCB) = [-accb-]/[a]_{sto} \tag{6e}$$

$$(BCCB) = [-bccb-]/[a]_{sto} \tag{6f}$$

The rate equations can be further simplified by the introduction of a dimensionless time variable, θ, such that

$$\theta = [a]_{sto}k_{aX}t \tag{7}$$

The rate of addition of XabX or YccY can be written as

$$d[XabX]_{added}/dt \text{ and } d[YccY]_{added}/dt$$

Letting

$$\frac{dXX}{dt} = \frac{1}{[a]_{sto}}\frac{d[XabX]_{added}}{dt} \tag{8a}$$

and

$$\frac{dYY}{dt} = \frac{1}{[a]_{sto}}\frac{d[YccY]_{added}}{dt} \tag{8b}$$

the substitution for time then yields the two dimensionless feed functions

$$\frac{dXX}{d\theta} = \frac{1}{[a]_{sto}^2k_{aX}}\frac{d[XabX]_{added}}{dt} \tag{9a}$$

and

$$\frac{dYY}{d\theta} = \frac{1}{[a]_{sto}^2k_{aX}}\frac{d[YccY]_{added}}{dt} \tag{9b}$$

Thus the system can be represented by the following set of first-order differential equations:

$$d(A)/d\theta = -2(A)(CC) - g_a(A)(ACC) - g_b(A)(BCC) + dXX/d\theta \tag{10a}$$

$$d(B)/d\theta = -2r(B)(CC) - 2rg_a(ACC)(B) - rg_b(B)(BCC) + dXX/d\theta \tag{10b}$$

$$d(CC)/d\theta = -2(A)(CC) - 2r(B)(CC) + dYY/d\theta \tag{10c}$$

$$d(ACC)/d\theta = 2(A)(CC) - g_b(A)(BCC) - rg_a(B)(ACC) \tag{10d}$$

$$d(BCC)/d\theta = 2r(B)(CC) - g_b(A)(BCC) - rg_b(B)(BCC) \tag{10e}$$

$$d(ACCA)/d\theta = g_a(ACC)(A) \tag{10f}$$

$$d(BCCB)/d\theta = rg_b(BCC)(B) \tag{10g}$$

$$d(ACCB)/d\theta = rg_a(ACC)(B) + g_b(BCC)(A) \tag{10h}$$

This system of equations becomes homogeneous when $dXX/d\theta = dYY/d\theta = 0$, e.g., at $\theta > 0$ if the two monomers are mixed together infinitely fast at the beginning of the polymerization. The set of equations were numerically integrated (and in some cases analytically solved) for the different addition modes. Important mathematical features of the three addition modes are as follows: mode 1, infinitely fast addition; after the beginning of the reaction $dXX/d\theta = dYY/d\theta = 0$ and $(A) = (B) = (CC) = 1$; modes 2 and 3, infinitely slow addition of XabX or YccY; dXX and dYY are not zero. An easy example is slow addition of YccY such that there will never be more than infinitesimal amounts of chains with -cY ends making $d(A) + d(B) = -2(dYY)$. For constant finite rate of addition of XabX to YccY, one obtains $dXX/d\theta = C_1$; for YccY to XabX, similarly one obtains $dYY/d\theta = C_2$.

The system (eq 10) becomes exceedingly stiff as $r \to 0$ and g_a, $g_b \to 0$. The routine employed for numerical integration was specific to situations that are stiff initial value problems: the NAG Library subroutine D02QBF uses a variable-order variable-step Gear's method.[32,33]

For linear polymers, the number-average degree of polymerization, $\bar{x}_n$, is defined as follows:

$$\bar{x}_n = \frac{2(\text{total number of monomeric units})}{\text{number of chain ends}} \tag{11}$$

Let N_{sto} denote the total number of monomeric units present in the system at the end of the polycondensation, and $N(\theta)$, the total number of monomeric units at a given dimensionless time θ. Then

$$N(\theta) = N_{\mathrm{sto}} \int_0^{\theta} [\mathrm{dXX} + \mathrm{dYY}]\, \mathrm{d}\theta' = \mathrm{XX} + \mathrm{YY} \quad (12)$$

where XX and YY are, respectively, the total amounts of ab and cc units present in the system at any given time. The number of chain ends is

$$N_{\text{chain ends}} = N_{\mathrm{sto}}[(\mathrm{A}) + (\mathrm{B}) + 2(\mathrm{C})] \quad (13)$$

Thus, $\bar{x}_{\mathrm{n}}$ becomes

$$\bar{x}_{\mathrm{n}} = 2[\mathrm{XX} + \mathrm{YY}]/[(\mathrm{A}) + (\mathrm{B}) + 2(\mathrm{C})] \quad (14)$$

The difference between (acca) and (bccb) at any given time is Δ and is given by

$$\Delta = ([\mathrm{acca}] - [\mathrm{bccb}])/([\mathrm{acca}] + [\mathrm{accb}] + [\mathrm{bccb}])$$

or

$$\Delta = [(\mathrm{B}) - (\mathrm{A})]/[2 - (\mathrm{A}) - (\mathrm{B})] \quad (15)$$

Results of the Integration of Kinetic Equations

The extreme mixing modes, infinitely fast or infinitely slow addition of one monomer to the other, will be discussed first. Note that, as was mentioned earlier, one cannot expect any constitutionally ordered polymers, if the chain-forming reaction does not distinguish between the two functional groups, -aX and -bX, of the nonsymmetric monomer regardless of any possible induction on both the nonsymmetric and symmetric polymers. A value of unity for r will always give rise to $s = 0.5$. A value of $r < 1$ is, therefore, a prerequisite in all further considerations.

Cases Where Feed Rates Need Not Be Considered. (i) *When functional groups on the symmetric monomer are independent, i.e.,* $g_{\mathrm{a}} = g_{\mathrm{b}} = 1$. In this case, no induction in the symmetric monomer is possible. Thus, the reaction can only be constitutionally controlled by r and the mode of addition of the reactants. Below, we evaluate the effects of the mixing modes outlined earlier. It will be seen that $s = s(r)$ and $0 \leq s \leq 0.5$. We distinguish three situations:

(*i.a*) *"All at Once"*. If XabX monomers are mixed infinitely fast with YccY monomers, then only disordered polymer chains can be formed. The faster reacting (-aX) group will react first, but, since all -cY groups are present in the system and no activating or deactivating induction is involved, only disordered intermediates will be formed and, thus, only disordered polymers can be obtained.

(*i.b*) *The nonsymmetric monomer is added to the symmetric monomer.* If XabX units are added infinitely slowly to the YccY monomers, then both -aX and -bX units will react at the same (concentration-dependent) rate. This again yields a completely disordered polymer.

(*i.c*) *The symmetric monomer is added to the nonsymmetric monomer.* When YccY monomers are added infinitely slowly to XabX monomers, then constitutional order is possible. This happens because -cY groups, which are present only in a very small amount because of the slow addition rate, react preferentially with -aX units first. If r is low, XbaccabX will be preferentially formed, and when all -aX units have been exhausted, the reaction of the remaining -bX units forces head-to-head/tail-to-tail order ($s \rightarrow 0$).

In summary one notes that no matter what the value of r is, if XabX and YccY are mixed together at the beginning of the reaction or if XabX is added to the reaction mixture containing YccY, only polymers of $s = 0.5$ can be obtained. The value of r greatly affects s for the case where YccY is being slowly added to XabX. The lower the value of r, the greater the degree of head-to-head/tail-to-tail ordering.

(*ii*) *When functional groups in the symmetric monomer have interdependent reaction rates but equal induction, i.e.,* $g_{\mathrm{a}} = g_{\mathrm{b}} \neq 1$. We distinguish two situations:

(*ii.a*) *"All at Once"*. When XabX and YccY are mixed infinitely fast and there is induction, then constitutional order is achievable through either of the following two mechanisms. If r is sufficiently small and the second reacting group on the YccY monomer is deactivated after the first has reacted (i.e., $g_{\mathrm{a}} = g_{\mathrm{b}} \leq 0$), then s will approach unity. This happens because the fast reacting -aX sites will cause a deactivating effect on the symmetric monomer. This forces the formation of XbaccY molecules as an early intermediate (a pseudomonomer of the type ab). Further reaction thus forces head-to-tail ($s \rightarrow 1$) order. If the induction is activating (i.e., $g_{\mathrm{a}} = g_{\mathrm{b}} > 1$), then s will approach zero. In this case the XbaccabX intermediate is formed preferentially. Sample cases of s as a function of g_{a} are shown in Figure 2. From this analysis, $s = s(r, g_{\mathrm{a}})$ and $0 \leq s \leq 1$.

(*ii.b*) *One monomer is added to the other.* If XabX is added infinitely slowly to YccY or YccY is added infinitely slowly to XabX, one does not take advantage of the induction on the YccY monomer. Thus, the results of these cases are identical with those discussed above.

(*iii*) *When functional groups in the symmetric monomer have interdependent reaction rates but unequal induction, i.e.,* $g_{\mathrm{a}} \neq 1, g_{\mathrm{a}} \neq g_{\mathrm{b}}$. For the extreme addition rates considered in this section ("infinitely slow" or "all at once"), values of polymer order are similar to those of the preceding case, except that, for values of $r \ll 1$, only the value of g_{a} affects the constitution. This is true since constitution in these cases is controlled by the -aX reacting groups (which react faster than -bX) and therefore is only greatly affected by -accY groups.

For some specific cases of these extreme addition rates, analytical solutions can be derived. For infinitely slow addition of YccY to XabX, for all values of r, g_{a}, and g_{b}, one can rederive Suter and Pino's[14] analytical approximation to the value of s at $1/\bar{x}_{\mathrm{n}} \rightarrow 0$. This relation holds within 2% for $r < 0.1$.

$$s \approx 1 - r^{r/(1-r)} \qquad 1/\bar{x}_{\mathrm{n}} \rightarrow 0 \quad (16)$$

For immediate mixing two expressions can be derived. For $r \neq 0$, $g_{\mathrm{a}} = g_{\mathrm{b}} = 0$, and $1/\bar{x}_{\mathrm{n}} = 0$, an implicit equation can be derived in s and r.

$$[(1-s)/2]^{1/(1+r)} + [(1-s)/2]^{r/(1+r)} - 1 = 0 \qquad g_{\mathrm{a}} = g_{\mathrm{b}} = 0, \quad 1/\bar{x}_{\mathrm{n}} \rightarrow 0 \quad (17)$$

For $r = 0$, $g_{\mathrm{a}} \neq 0$, and $1/\bar{x}_{\mathrm{n}} = 0$, another implicit expression can be derived:

$$[(1-s)/2]^{g_{\mathrm{a}}/2} + (1-g_{\mathrm{a}})(1-s)/2 - (2-g_{\mathrm{a}})/2 = 0 \qquad r = 0, \quad 1/\bar{x}_{\mathrm{n}} \rightarrow 0 \quad (18)$$

Since the value of g_{b} is of minor importance in these cases, eq 16 and 17 can be employed with a modest loss in accuracy also to cases where $g_{\mathrm{a}} \neq g_{\mathrm{b}}$. Equations 16–18 can be used to provide a check of the numerical integration results. Table II compares results obtained from the

Table II
Comparison between Equations 16–18 and the Numerical Integration Technique

YccY Added Infinitely Slowly to XabX

	s	
	numerical integration[a] ($1/\bar{X}_n \leq 0.01$)	eq 15 ($1/\bar{X}_n = 0$), ±2%
$r = 0.1$, $g_a = g_b = 1$	0.225 ± 0.005	0.23
$r = 0.01$, $g_a = g_b = 1$	0.046 ± 0.005	0.05
$r = 0.01$, $g_a = g_b = 0.01$	0.048 ± 0.005	0.05
$r = 0.01$, $g_a = 1$, $g_b = 0.01$	0.049 ± 0.005	0.05
$r = 0.01$, $g_a = 0.01$, $g_b = 1$	0.050 ± 0.005	0.05

YccY and XabX Mixed Infinitely Fast

	s	
	numerical integration[a] ($1/\bar{X}_n \leq 0.01$)	eq 16 ($1/\bar{X}_n = 0$)
$r = 1$, $g_a = g_b = 10^{-5}$	0.490 ± 0.005	0.50[b]
$r = 0.01$, $g_a = g_b = 10^{-5}$	0.934 ± 0.005	0.94[b]
$r = 0.01$, $g_a = 10^{-5}$, $g_b = 0.01$	0.970 ± 0.005	0.94[b]
$r = 0.01$, $g_a = 10^{-5}$, $g_b = 1$	0.975 ± 0.005	0.94[b]

	s	
	numerical integration ($1/\bar{X}_n \leq 0.01$)	eq 17 ($1/\bar{X}_n = 0$)
$r = 10^{-5}$, $g_a = g_b = 0.01$	0.967 × 0.005	0.97[c]
$r = 10^{-5}$, $g_a = 0.01$, $g_b = 1$	0.968 ± 0.005	0.97[c]

[a] The indicated limits are estimates of confidence limits from the preset numerical integration tolerance. [b] Equation 16 implies $g_a = 0$. [c] Equation 17 implies $r = 0$.

numerical integration method with those obtained from these equations.

Finite Feed Rates. The model described in the previous sections can be used with any type of finite rate addition; for example, constant feed rate, stepwise addition, etc. In this section results of constant rates of addition of YccY to XabX and XabX to YccY are examined. A constant rate of addition is attractive because one would be able to continuously vary the feed rate from the "infinitely slow" extreme case to the "all at once" extreme. Also, this method is easily employed both in laboratory and in larger scale applications. Constant rates of addition of one monomer to the other are quantified by the dimensionless parameters dXX/dθ (XabX added to YccY) and dYY/dθ (YccY added to XabX).

(*i*) *When functional groups are independent*; *i.e.*, $g_a = g_b = 1$. Figure 3 depicts a series of cases for s as a function of dXX/dθ and dYY/dθ for various values of r. In all cases the final degree of polymerization is 100. As shown, the polymer order, s, varies continuously from "very slow" to "very fast" addition, and quite steeply in between when YccY is added to XabX. When XabX is added to YccY, one always obtains a disordered polymer, which is consistent with the previous discussion. Thus polymer order can easily be controlled from the maximum to the minimum possible s given the kinetic parameters; $s = s(r,\text{feed rate})$.

(*ii*) *When functional groups are interdependent but have equal induction*; $g_a = g_b \neq 1$. Figure 4 depicts the effect of changes in g_a (and g_b) for both types of addition at a constant value of $r = 0.01$. For $g_a = g_b = 0.01$, varying the addition rate of the YccY monomer to XabX monomer controls constitution in a range from $s = 0.049$ to $s = 0.945$. This represents a change from a structure that is almost completely head-to-head/tail-to-tail to one that is mostly head-to-tail. Varying the rate of addition influences

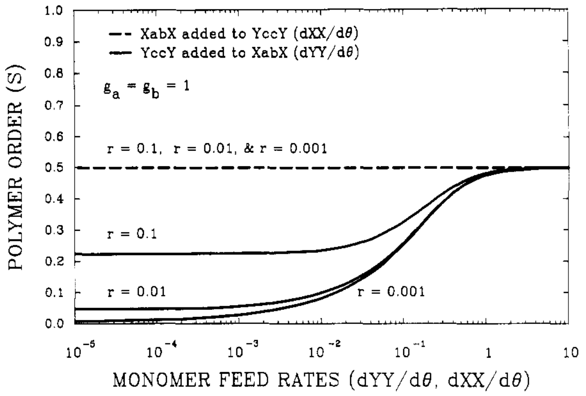

Figure 3. s as a function of monomer feed rates (—) dYY/dθ (YccY is fed continuously) and (- - -) dXX/dθ (XabX is fed continuously) at various values of r. The functional groups on the YccY monomer are independent of each other ($g_a = g_b = 1$).

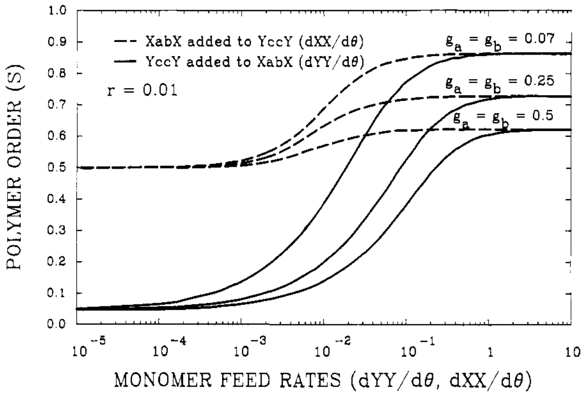

Figure 4. s as a function of monomer feed rates (—) dYY/dθ (YccY is fed continuously) and (- - -) dXX/dθ (XabX is fed continuously) at $r = 0.01$. The functional groups on the YccY monomer are dependent upon each other but show equal degrees of induction ($g_a = g_b \neq 1$).

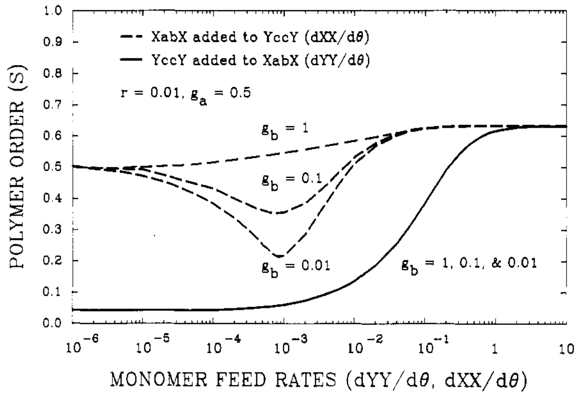

Figure 5. s as a function of monomer feed rates (—) dYY/dθ (YccY is fed continuously) and (- - -) dXX/dθ (XabX is fed continuously) at $r = 0.01$. The functional groups on the YccY monomer are dependent upon each other and show unequal degrees of induction ($g_a = 0.5$, g_b varies).

s. However, the maximum value of s, i.e., the highest order of the head-to-tail type, is achieved with "infinitely fast addition". Again, the extreme cases of these results are consistent with the previous discussion on limiting cases of addition rates.

(*iii*) *When functional groups have interdependent reaction rates but unequal induction*; *i.e.*, $g_a \neq 1$, $g_a \neq g_b$. In the previous discussion on extreme addition rates it was noted that in all cases where induction was present only the value of g_a caused changes in polymer constitution. For finite feed rates this is no longer always true. As shown in Figure 5, when YccY is added to XabX, the results are

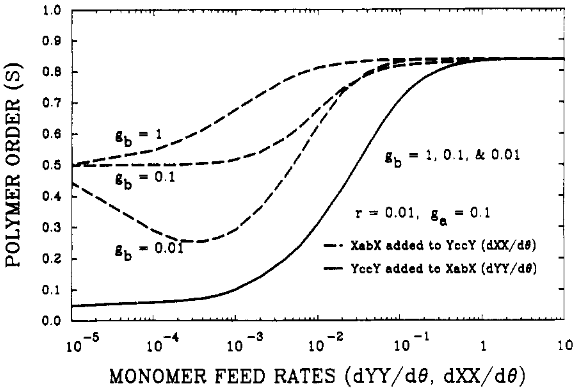

Figure 6. *s* as a function of monomer feed rates (—) dYY/dθ (YccY is fed continuously) and (- - -) dXX/dθ (XabX is fed continuously) at $r = 0.01$. The functional groups on the YccY monomer are dependent upon each other and show unequal degrees of induction ($g_a = 0.1$, g_b varies).

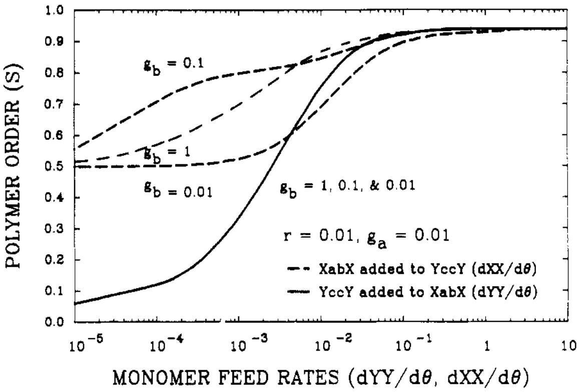

Figure 7. *s* as a function of monomer feed rates (—) dYY/dθ (YccY is fed continuously) and (- - -) dXX/dθ (XabX is fed continuously) at $r = 0.01$. The functional groups on the YccY monomer are dependent upon each other and show unequal degrees of induction ($g_a = 0.01$, g_b varies).

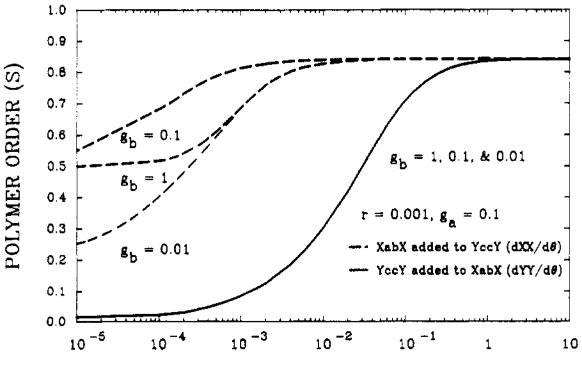

Figure 8. *s* as a function of monomer feed rates (—) dYY/dθ (YccY is fed continuously) and (- - -) dXX/dθ (XabX is fed continuously) at $r = 0.001$. The functional groups on the YccY monomer are dependent upon each other and show unequal degrees of induction ($g_a = 0.1$, g_b varies).

identical with the equal induction situation with respect to changes in g_a, as expected from reasons already discussed. However, when XabX is added to YccY, values of *s* much lower than the previous minimum of 0.5 are obtained at slow (but not "infinitely" slow) feed rates. The cause for this is the formation of more –bccY units than in either of the two extremes. These units have a deactivating induction lower than that of –accY units, and this causes more head-to-head/tail-to-tail alignment due to the YccabccY units reacting preferentially on the Ycca– side. Further examples of this are shown in Figure 6–8. Note that only the proper combinations of *r*, g_a, g_b, and feed rate of XabX will cause this phenomena.

Table III
Constitutionally Ordered and Disordered Polyureas from 1 and 2[a] (Experimental Data from Reference 22)

method of preparn	$[\eta]^b$	$\bar{M}_n$	$\bar{X}_n$	*s* expt[c]	*s* calc[d]
1 added slowly to 2	0.38	3700	45	0.05	<0.01
1 and 2 mixed rapidly	0.33	1700	21	0.89	0.98
2 added slowly to 1	0.57	4300	53	0.47	0.50

[a] Monomer 1: bis(*p*-nitrophenyl) carbonate. Monomer 2: 2-(4-aminophenyl)ethylamine. [b] In units of deciliters per gram; in DMSO/LiCl (2%) at 30 °C. [c] ^{1}H NMR in DMSO-d_6/LiCl (2%) at 120 °C (90 MHz) or ^{13}C NMR in DMSO-d_6/LiCl (5%) at 30 and 50 °C (22.6 MHz). [d] Calculation performed by using $\bar{X}_n = 100$, $r = 6.3 \times 10^{-6}$, $g_a = 3.6 \times 10^{-5}$, and $g_b = 1$.

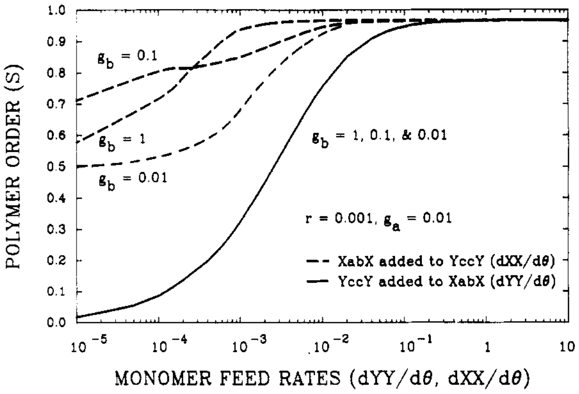

Figure 9. *s* as a function of monomer feed rates (—) dYY/dθ (YccY is fed continuously) and (- - -) dXX/dθ (XabX is fed continuously) at $r = 0.001$. The functional groups on the YccY monomer are dependent upon each other and show unequal degrees of induction ($g_a = 0.01$, g_b varies).

Comparison to Experiment

Polyureas were obtained in high order from bis(*p*-nitrophenyl) carbonate (1) and 2-(4-aminophenyl)ethylamine (2) by Schmucki et al.[22] From the data they presented on model compounds, one can calculate that $r = 6.3 \times 10^{-6}$, $g_a = 3.6 \times 10^{-5}$, and $g_b \approx 1$. A comparison of results obtained from experimental data and the model calculations is shown in Table III. The value of *s* as a function of dXX/dθ and dYY/dθ is plotted in Figure 10. Note that one can easily change the constitutional order of this polymer from almost completely head-to-head/tail-to-tail to almost completely head-to-tail. Table IV summarizes the influence of kinetic parameters and mixing mechanisms on polymer constitutional order.

Monte Carlo Polycondensation

Additional information on the polymer structure can be obtained by Monte Carlo calculations. This type of simulation also provides a check of the numerical integration method as well as analysis of systems in greater detail. As stated, *s* is determined by the frequency of –acca–, –accb–, and –bccb– "diad" units in the polymer, the smallest arrangements with distinguishable orientation. In order to determine if *s* is a sufficient parameter to completely characterize the polymer, one would need information on the next level of description of structure. This level would involve "triad" species, i.e., arrangements like –accabcca–, –accabccb–, etc. If polymers of equivalent *s* also have comparable triad fractions, then the value of *s* could be exclusively used to describe the polymer structure. This is particularly important when comparing polymers of equal *s*, synthesized from the same monomers

Table IV
Kinetic Control of Constitutional Isomerism ($1/\bar{X}_n \rightarrow 0$)

- Extreme Addition Rates (Very Slow or Very Fast)
    - *Functional Groups in the Symmetric Monomer Are Independent*: $g_a = g_b = 1$ ($0 \leq s \leq 0.5$)
        - YccY slowly added to XabX: $s = s(r)$
        - XabX slowly added to YccY or immediate mixing of reactants: $s = 0.5$
    - *Functional Groups in the Symmetric Monomer Are Interdependent*: $g_a, g_b \neq 1$ ($0 \leq s \leq 1$)
        - YccY slowly added to XabX: $s = s(r)$ (just as above!)
        - XabX slowly added to YccY: $s = 0.5$ (just as above)
        - Immediate mixing of reactants: $s = s(g_a,r)$; $g_a \rightarrow 0$, $s \rightarrow 1$; $g_a \rightarrow \infty$, $s \rightarrow 0$
- Finite Feed Rates
    - *Functional Groups in the Symmetric Monomer Are Independent*: $g_a = g_b = 1$ ($0 \leq s \leq 0.5$)
        - YccY added to XabX: $s = s(r,\text{feed rate})$
        - XabX added to YccY: $s = 0.5$
    - *Functional Groups in the Symmetric Monomer Are Interdependent*: $g_a, g_b \neq 1$ ($0 \leq s \leq 1$)
        - YccY added to XabX: $s = s(r,g_a,\text{feed rate})$
        - XabX added to YccY: $s = s(r,g_a,g_b,\text{feed rate})$

but via different synthetic routes as illustrated in the previous section.

Basic Formalism. In the Monte Carlo method one simulates the reaction between a large number of monomer molecules of each type (e.g., 200 000 monomers total). The six elementary reactions illustrated earlier can be converted to rate equations. When N_i denotes the number of species of type i in the system, the rate of each elementary reaction (eqs 4a–4f) becomes

$$\text{rate of reaction a} = 2N_{\text{-aX}}N_{\text{YccY}} \tag{19a}$$

$$\text{rate of reaction b} = 2rN_{\text{-bX}}N_{\text{YccY}} \tag{19b}$$

$$\text{rate of reaction c} = g_aN_{\text{-aX}}N_{\text{-accY}} \tag{19c}$$

$$\text{rate of reaction d} = rg_aN_{\text{-bX}}N_{\text{-accY}} \tag{19d}$$

$$\text{rate of reaction e} = g_bN_{\text{-aX}}N_{\text{-bccY}} \tag{19e}$$

$$\text{rate of reaction f} = rg_bN_{\text{-bX}}N_{\text{-bccY}} \tag{19f}$$

Monomer addition rates for XabX and YccY become "reactions" number g and h such that

$$\text{rate of reaction g} = k_{\text{aX}}' = \frac{\mathrm{d}N_{\text{XabX,added}}}{\mathrm{d}t} \tag{19g}$$

$$\text{rate of reaction h} = k_{\text{aX}}' = \frac{\mathrm{d}N_{\text{YccY,added}}}{\mathrm{d}t} \tag{19h}$$

Note that reactions g and h are dimensionally the same as a–f. This is made possible by changing the units of the rate constant; $k_{\text{-aX}}'$ is in units of number of groups per unit time. The relationship between these "reaction rates" and the dimensionless monomer feed rates, $\mathrm{dXX}/\mathrm{d}\theta$ and $\mathrm{dYY}/\mathrm{d}\theta$, developed in the numerical integration method is

$$\frac{\mathrm{d}N_{\text{XabX,added}}}{\mathrm{d}t} = \frac{\mathrm{dXX}}{\mathrm{d}\theta}k_{\text{-aX}}'[(N_{\text{-ab-total}} + N_{\text{-cc-total}})/2]^2 \tag{20a}$$

and

$$\frac{\mathrm{d}N_{\text{YccY,added}}}{\mathrm{d}t} = \frac{\mathrm{dYY}}{\mathrm{d}\theta}k_{\text{-aX}}'[(N_{\text{-ab-total}} + N_{\text{-cc-total}})/2]^2 \tag{20b}$$

where the subscript "total" denotes the total number of –ab– units and –cc– units when equimolarity is reached, i.e., after all units have been added.

During the course of the simulation of the polymerization reaction, the number of chain ends, diads, and triads formed are counted. Once the reaction is completed, we can calculate the polymer order and the degree of "blockyness" of the chains. The reaction is complete when the desired degree of polymerization is reached.

For cases where all monomers are present at the beginning of the polymerization, there are 100 000 XabX and 100 000 YccY monomers. The rates of reactions a–f are converted into probabilities, and a uniform random number[34] is used to select which reaction occurs at each step. After the selection, counters that keep track of all species involved in the reaction are either diminished or augmented. The process continues until the reaction is complete. When a finite feed rate is used, reaction g or h can be selected. In these cases the proper monomeric species are incremented by one until all the monomer has been added. Reactions c–f form diad species, and these are used to determine the value of s. At this point the global polymer order, s, can be calculated. Here s is given by

$$s = [N_{\text{accb}} + N_{\text{bcca}}]/[N_{\text{acca}} + N_{\text{accb}} + N_{\text{bcca}} + N_{\text{bccb}}] \tag{21}$$

For the calculation of triad species, one proceeds as follows. There are eight triad species possible in the polymer chain that can be envisioned. However, due to symmetry, only four species can be distinguished. The eight structures grouped together in four distinguishable sets are listed.

–accabccb– and –bccbacca–

–accbacca– and –accabcca–

–bccabccb– and –bccbaccb–

–bccabcca– and –accbaccb–

The triad calculation only occurs if reaction c, d, e, or f occurs. Recall that reaction c forms an –acca– diad, d an –accb–, e a –bcca–, and f a –bccb–. The calculation for triads involves determining whether or not another diad is attached to a side of the newly formed diad. This is done by determining the probabilities of all possible species that can be attached on both sides and deciding what is indeed attached by another Monte Carlo choice. If a triad is formed, the triad counters are incremented accordingly. Triad calculations can occur for any method of adding monomers to the reaction mixture.

Results and Discussion of the Monte Carlo Method

Comparison to Numerical Integration Method. For all cases for which the numerical integration method yields

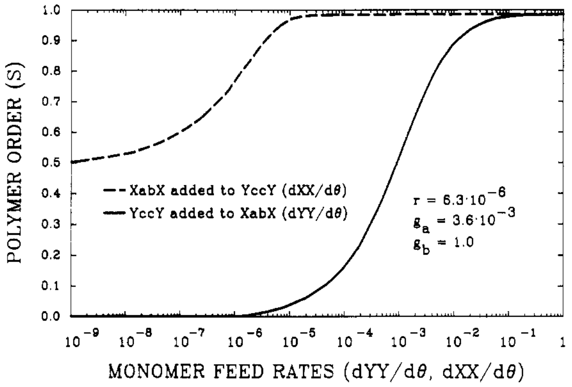

Figure 10. *s* as a function of monomer feed rates (—) dYY/dθ (YccY is fed continuously) and (- - -) dXX/dθ (XabX is fed continuously) for polyurea polycondensation (see text for details).

Table V
Comparing Polymers with Equal *s*, Prepared Differently from the Same Monomers ($r = 1 \times 10^{-2}$, $g_a = 0.5$, $g_b = 0.1$, $1/\bar{X}_n \to 0$)

triad	fraction (±0.02)	triad	fraction (±0.02)
Polymer PI: XabX Added to YccY (dXX/dθ = 1×10^{-5})			
–accabccb– –bccbacca–	0.26	–bccabccb– –bccbaccb–	0.24
–accbacca– –accabcca–	0.27	–bccabcca– –accbaccb–	0.23
Polymer PII: YccY Added to XabX (dYY/dθ = 2×10^{-1})			
–accabccb– –bccbacca–	0.33	–bccabccb– –bccbaccb–	0.17
–accbacca– –accabcca–	0.18	–bccabcca– –accbaccb–	0.32

solutions for the relative number of diad species, the Monte Carlo method provides an almost identical answer. The solutions agree to within ±0.02 (this is the estimated 2σ confidence limit of the Monte Carlo average).

Triad Formation. Triad formation calculations show that *s* is sometimes not sufficient to completely describe the polymer chain. An example is shown in Table V. Two hypothetical polymers, PI and PII, were made from monomers that react with the kientic parameters $r = 0.01$, $g_a = 0.5$, and $g_b = 0.1$ to a final degree of polymerization of 100. Polymer PI was made by the very slow addition of XabX to YccY, while polymer PII was generated by a much faster addition of YccY to XabX. Polymer PI is very disordered, having nearly equal amounts of possible triads, while polymer PII is much less disordered (it shows a tendency toward –accbaccb– and –accabccb– blocks). Thus, diad statistics as expressed by *s* may not always be sufficient to describe a polymer with nonsymmetric units.

Summary and Conclusions

This work indictaes that, in answer to the question posed at the beginning of this work, constitutional isomerism in step polymerization can be controlled in an easy and preselectable manner. It has been shown that high degrees of order can only be obtained via kinetically controlled reactions and that the same single reaction step can be used to generate polymers of continuously differing order, within the limits set by the relative reaction rate constants, i.e., r, g_a, and g_b.

In general, if the symmetric monomer (YccY) is fed very slowly to the reaction mixture containing all of the nonsymmetric monomer (XabX), the highest possible head-to-head/tail-to-tail regularity is achieved. If the nonsymmetric monomer (XabX) is added very slowly to the reaction mixture containing all of the symmetric monomer (YccY), a random polymer is invariably obtained. Finally, if the reactants are mixed all at once ("infinitely fast"), the highest possible degree of head-to-tail constitution is achieved; this might, however, only be as high as the random case; i.e., if no interdependence of functional groups exists, no significant head-to-tail regularity can be obtained.

If an interdependence of functional groups that are unequal exists and the XabX monomer is added to the YccY monomer in a slow but not very slow manner, then the constitutional order is goverened by all kinetic parameters and cases of high head-to-head/tail-to-tail order are possible.

The constitutional regularity of macromolecules from step-growth polymerizations is succinctly expressed by *s*, the probability of two adjacent nonsymmetric monomeric units pointing in the same direction along the chain. It is, however, possible to obtain polymers from different one-stage syntheses that are characterized by the same *s* but have clearly different constitutional statistics. In that case, information on the next level of refinement is needed and can be obtained through a Monte Carlo analysis.

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