

Microtacticity Changes During Transesterification

Nikolay A. Platé[†], Arkady D. Litmanovich, Yaroslav V. Kudryavtsev, Konstantin V. Demidenok

*A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,
Leninsky Prospekt, 29, Moscow B-71, 119991 Russia*

Received 11 March 2006; accepted 24 May 2006

DOI 10.1002/app.26089

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effect of a direct interchain exchange reaction (transesterification) on the microtacticity of polymer chains is studied with theory and a Monte Carlo simulation. Kinetic equations describing the evolution of the distribution over the type and length of the dyad sequences in the course of transesterification are derived. From this detailed consideration, the dependence of the average lengths of the isotactic and syndiotactic sequences on time is calculated for a melt of an initially isotactic homopolymer. It is shown that the microtacticity change proceeds at a rate similar to that of copolymer randomization during transesterification in polymer blends and much more

slowly than the relaxation of the molecular mass distribution. The reacting chains for a long time consist of isotactic sequences of decreasing length and mostly isolated syndiotactic dyads. Possible effects of varying the ratio of the rate constants of the elementary reactions between dyads of different types are investigated. The agreement between the calculations and results of the Monte Carlo simulation is satisfactory. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 60–66, 2007

Key words: esterification; microstructure; Monte Carlo simulation; stereospecific polymers; theory

INTRODUCTION

The mutual orientation of side groups along a polymer chain (microtacticity) is an important factor that makes chemically identical macromolecules different in their reactivity and physical properties, such as their crystallinity and biodegradability. Correlations in side-group positions (stereoregularity) arising in the course of polymer synthesis can be afterwards affected by macromolecular reactions. Interchain exchange (interchange) is a very common reaction that accompanies the synthesis and processing of condensation polymers and results in the random redistribution of unit sequences between different macromolecules. In blends, it leads to the formation of copolymers and may be desirable or not, depending on the type and aim of processing.

The evolution of the molecular mass and block length distributions during interchange reactions has

been extensively studied both theoretically and experimentally.^{1,2} Practically useful approaches have been suggested that make it possible to quantitatively interpret data of NMR,^{3,4} neutron scattering,⁵ X-ray scattering,⁶ and mass spectrometry⁷ related to reacting systems. Interchange reactions are incorporated into a general computational scheme for modeling polycondensation kinetics.⁸ However, no methods have so far been proposed to describe the influence of interchanges on the polymer microtacticity, even though that effect obviously takes place. For example, a ¹H- and ¹³C-NMR study of transesterification in the course of the stereoselective polymerization of lactides⁹ has demonstrated that in late stages of the reaction, the microtacticity of a biodegradable polymer that is formed is affected by interchange reactions, whereas in early stages, it is mostly determined by the type of initiator.

The purpose of this study is to develop a computational method describing the evolution of polymer microtacticity during interchange reactions. The approach is based on our recent theoretical studies of interchange kinetics in polymer blends.^{10,11} To demonstrate its applicability, the interchange in an initially isotactic homopolymer melt is considered, and the results are checked by a Monte Carlo simulation.

MODEL

Consider a homopolymer melt of M chains. Let each repeating unit contain a side group characterized by one of two spatial configurations, which we denote as \uparrow and \downarrow . Neighbor units belonging to one chain and possessing the same configuration ($\uparrow\uparrow$ or $\downarrow\downarrow$) form an

This article is dedicated to the memory of Professor Marian Kryszewski.

Correspondence to: Y. V. Kudryavtsev (yar@ips.ac.ru).

Contract grant sponsor: Russian Fund for Basic Research; contract grant number: 02-03-33088.

Contract grant sponsor: Program of the President of the Russian Federation for Young Scientists and Leading Research Schools; contract grant number: MD-4684.2006.3.

Contract grant sponsor: Russian Science Support Foundation (to Y.V.K.).

Contract grant sponsor: Netherlands Organization for Scientific Research; contract grant number: NWO 047.019.003 to (Y.V.K.)

[†]Suddenly diseased on March 16, 2007.

Journal of Applied Polymer Science, Vol. 105, 60–66 (2007)
© 2007 Wiley Periodicals, Inc.



isotactic dyad (I), whereas neighboring units of different configurations ($\uparrow\downarrow$ or $\downarrow\uparrow$) add up to a syndiotactic dyad (S). Dyads constitute sequences; for example, $\uparrow\uparrow\uparrow$ is an isosequence of length 3 (in dyads), whereas $\uparrow\downarrow\downarrow\uparrow\downarrow\uparrow$ is a syndiosequence of length 7. A sequence of dyads represents the microtacticity of any chain just as a unit sequence describes the structure of a binary copolymer. Consequently, a similar kinetic scheme may be used when we consider the effect of an interchange on the distribution of isodyad and syndiodiad sequences and on the unit distribution in copolymers.

Assume that an interchange reaction may take place between any two dyads neighboring in space. Such a transformation is called a direct interchange, and transesterification is an example. Reactions involving chain ends, such as acidolysis and alcoholysis, are not allowed in our system, but their consideration seems not very different from what we do here, just as in the case of direct and end-group interchanges in polymer blends.¹²

Consider reversible elementary reactions that change the dyad distribution. Four of them, depicted in Figure 1, are adopted as the most likely to occur. Five rate constants— k_{I1} (reaction I + I \rightarrow I + I), k_{I2} (I + I \rightarrow S + S), k_{IS} (I + S \rightarrow I + S), k_{S1} (S + S \rightarrow S + S), and k_{S2} (S + S \rightarrow I + I)—are equal to the probabilities (per unit of time) of the corresponding reactions between dyads neighboring in space.

In principle, some other elementary reactions are also possible, such as I + I \rightarrow I + S, but they require the rotation of the end that appears as a result of the chain cleavage, unlike the four reactions considered above. Hence, we infer that such reactions are much less probable and neglect them. If necessary, they can be included in the kinetic scheme in a standard way.

Note also that we consider interchange reactions between dyads rather than repeating units and neglect cyclization. It introduces an error of the order of the inverse of the number-average polymerization

degree ($1/\bar{N}$), but for long chains ($\bar{N} \gg 1$), such an error is small.

Kinetic considerations

The derivation of kinetic equations begins with choosing relevant variables. If a detailed description is needed, one has to consider the distribution of dyad sequences over their type and length. The solution of that problem is given in the appendix. However, usually only a few variables are practically important, that is, related to measurable quantities. In our case, these may be the average lengths of the iso- and syndiosequences (\bar{N}_I and \bar{N}_S , respectively). They are expressed through the total numbers of dyads (n), isosequences (m_I), and syndiosequences (m_S) and the total fraction of isotactic dyads (ϕ) as $\bar{N}_I = n\phi/m_I$ and $\bar{N}_S = n(1-\phi)/m_S$. Considering the effect of elementary reactions shown in Figure 1 on the dyad sequence population, we can easily write down the kinetic equations directly for the variables ϕ , m_I , and m_S :

$$\frac{1}{z} \frac{d\phi}{dt} = \frac{1}{2} \left(-k_{I2}\phi^2 + k_{S2}(1-\phi)^2 \right) \quad (1)$$

$$\begin{aligned} \frac{1}{z} \frac{dm_I}{dt} = n & \left(\frac{k_{I2}\phi^2}{2} + k_{IS}\phi(1-\phi) + \frac{k_{S2}(1-\phi)^2}{2} \right) \\ & - m_I(k_{I2}\phi + k_{IS}(1-\phi)) \\ & - \frac{m_I + m_S - M}{2} (k_{IS}\phi + k_{S2}(1-\phi)) \quad (2) \end{aligned}$$

$$\begin{aligned} \frac{1}{z} \frac{dm_S}{dt} = n & \left(\frac{k_{I2}\phi^2}{2} + k_{IS}\phi(1-\phi) + \frac{k_{S2}(1-\phi)^2}{2} \right) \\ & - m_S(k_{S2}(1-\phi) + k_{IS}\phi) \\ & - \frac{m_I + m_S - M}{2} (k_{IS}(1-\phi) + k_{I2}\phi) \quad (3) \end{aligned}$$

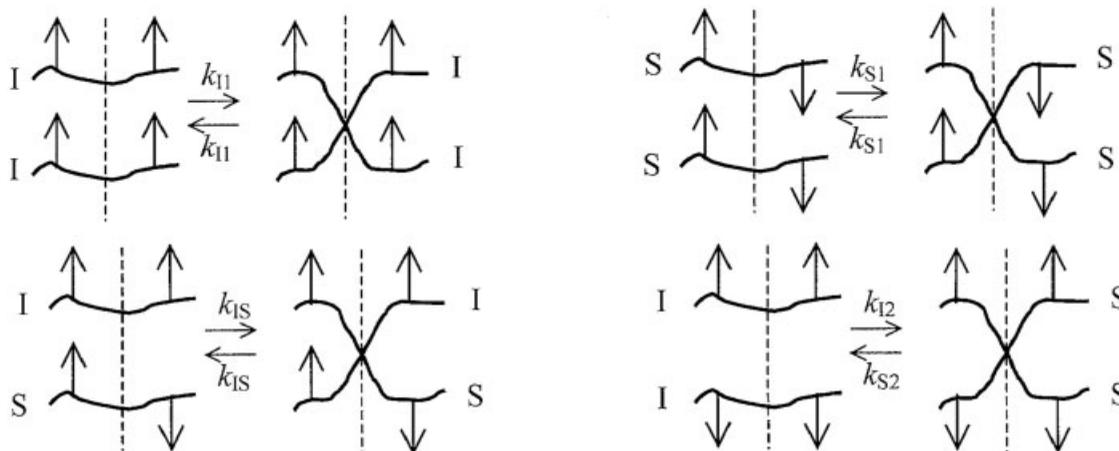


Figure 1 Elementary interchange reactions and their rate constants.

where z is the average number of dyads with which a chosen dyad may react at any moment of time. It is not necessary to specify z because it is included in the effective time (τ) introduced below. The first term in eqs. (2) and (3) reflects the formation of new iso- and syndiosequences, whereas the second and third terms account for the disappearance of existing sequences due to the interchange at their terminal dyads and dyads of the opposite kind flanking the sequences, respectively.

Equations (1)–(3) form a closed set, which may be solved provided that the rate constants, n and M , are known and the initial conditions are specified. Performing the solution, we can find the dependence of the average iso- and syndiosequence lengths on time, $\bar{N}_I(t)$ and $\bar{N}_S(t)$.

It is interesting to note that in the case of equal rate constants, $k_{I1} = k_{I2} = k_{IS} = k_{S1} = k_{S2} = k$, the considered model is equivalent to the model of the direct interchange in an equimolar blend of polymers A and B of the equal initial polymerization degree $\bar{N}_{A0} = \bar{N}_{B0}$, which is characterized by the single rate constant k . Indeed, a syndiodiad corresponds to dyad AB, whereas an isodyad corresponds to dyad AA or BB. It can therefore be shown that the equations for the total number of A sequences and AB dyads derived in ref. 10 may be obtained from eqs. (1)–(3) as well.

Monte Carlo simulation

A set of 10,000 macromolecules of an initial polymerization degree of 100 (99 dyads) is generated. Each macromolecule consists of blocks that are formed by monomer units of the same orientation (\uparrow or \downarrow), and the block lengths are stored. Such a description is equivalent to the dyad language: a block of length $i > 1$ is an isosequence of length $i - 1$, whereas a syndiosequence of i dyads is formed by $i - 1$ subsequent blocks of the unit length. Blocks are changed in the course of transesterification proceeding via the route shown in Figure 1.

The reaction is modeled as follows. The greatest constant among k_{I1} , k_{I2} , k_{IS} , k_{S1} , and k_{S2} is found and all rate constants are divided by that value to get the reduced rate constants lying in the interval (0, 1). Two different macromolecules and a dyad on each of them are arbitrarily chosen for the reaction. The kind of dyad (I or S) is determined, whereas the mutual orientation is specified at random. After that, the possible reaction route is unambiguous. A random number belonging to the interval (0, 1) is chosen and compared with the corresponding reduced rate constant. If the latter is greater, then the reaction takes place, and corresponding changes are made in the array of information. The conversion is measured in the number of cleavages per average macromolecule (of 100 units).

RESULTS AND DISCUSSION

Let us consider the case when all macromolecules are initially isotactic. Our purpose is to describe their loss of stereoregularity via transesterification. We will obtain the numerical solution of the kinetic equations [eqs. (1)–(3)] and carry out the corresponding Monte Carlo simulation.

It is seen that eq. (1) contains only variable ϕ , which is easily found in the explicit form $\phi(t) = [1 + \sqrt{k_{I2}/k_{S2}} \tanh(\sqrt{k_{I2}k_{S2}zt}/2)]^{-1}$. Then, the remaining equations, eqs. (2) and (3), may be considered as a set with respect to m_I and m_S . However, because there is no real time in a Monte Carlo simulation, it is more convenient to introduce an effective time (τ):

$$\tau = z \frac{n}{M} \int_0^t d\theta \left(2k_{IS}\phi(\theta)(1 - \phi(\theta)) + \frac{1}{2} \left((k_{I1} + k_{I2})\phi^2(\theta) + (k_{S1} + k_{S2})(1 - \phi(\theta))^2 \right) \right)$$

which is equal to the number of cleavages for a chain of $\bar{N} = n/M$ dyads by time t . As a result, eqs. (1)–(3) are transformed into a set of ordinary differential equations for variables $\phi(\tau)$, $m_I(\tau)/n$, and $m_S(\tau)/n$, which may be solved by numerical methods under the initial conditions $\phi(\tau = 0) = 1$, $m_I(0)/n = 1/99$, and $m_S(0)/n = 0$. For calculations, Maple software was used. The functions $\phi(\tau)$, $m_I(\tau)/n$, and $m_S(\tau)/n$ were evaluated at $0 \leq \tau \leq 100$ for different rate constant ratios.

Transesterification in an initially isotactic monodisperse system was also modeled by a Monte Carlo simulation as described above. Each numerical experiment was repeated several times to provide statistical noise damping, and the results were then averaged. It was found that the molecular mass distribution relaxed rapidly in agreement with theoretical predictions¹³ and reported simulation data¹⁴ and after ~ 10 cleavages per average chain converged to the most probable (Flory) distribution. The distribution of isotactic sequences over the length evolves much more slowly: although at $\tau \sim 10$ it also takes the form of the Flory distribution, its average is still much more than unity (Fig. 2). The complete loss of stereoregularity of the macromolecules requires each interchangeable bond to react on average once, which corresponds to $\tau \sim 100$. Note that the same degree of conversion is needed for the relaxation of the block length distribution in an initial blend of two homopolymers of 100 repeating units.^{10,15}

The dependence of the fraction of isodyads (ϕ), the average length of the isosequence ($\bar{N}_I = n\phi/m_I$), and the average length of the syndiosequence ($\bar{N}_S = n(1 - \phi)/m_S$) on τ is plotted in Figures 3–5, where curves 1–3 represent the results of numerical calculations for three rate constant sets: (1) $k_{I1}/k_{I2}/k_{IS}/k_{S1}/k_{S2} = 1$

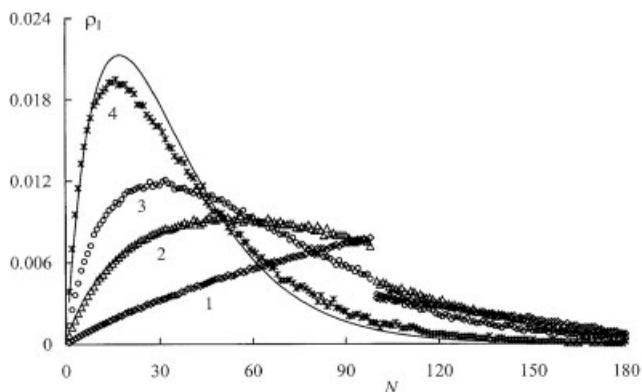


Figure 2 Evolution of the differential mass fraction of monomer units entering isotactic blocks of length N (ρ_I) in the course of transesterification. The point sets correspond to the different number of cleavages per average chain [$\tau = 1(1), 3(2), 5(3),$ and $10(4)$]. Unreacted chains at $N = 100$ are not shown. All rate constants are equal: $k_{I1} = k_{I2} = k_{IS} = k_{S1} = k_{S2}$. The curve corresponds to the Flory distribution with the same average block length as that at $\tau = 10$.

: 1 : 1 : 1 : 1 : 1, (2) $k_{I1}/k_{I2}/k_{IS}/k_{S1}/k_{S2} = 1 : 0.04 : 0.2 : 0.04 : 1$, and (3) $k_{I1}/k_{I2}/k_{IS}/k_{S1}/k_{S2} = 0.04 : 1 : 0.02 : 1 : 0.04$; the points are the data of the corresponding Monte Carlo simulation.

It is seen that the relative shortening of the isosequences (Fig. 4) proceeds much more intensively than the formation (Fig. 3) and growth of the syndiosequences (Fig. 5), especially in the early stages of the reaction (at $\tau < 10$).

If the formation of syndiodyads is hampered in comparison with that of isodyads, then the stereoregularity breakdown proceeds essentially more slowly (curves 2), whereas reducing the rate constants related to the formation of isodyads has a much less pronounced effect on the process (curves 3). The dependence of $\bar{N}_S(\tau)$ resembles straight lines until τ

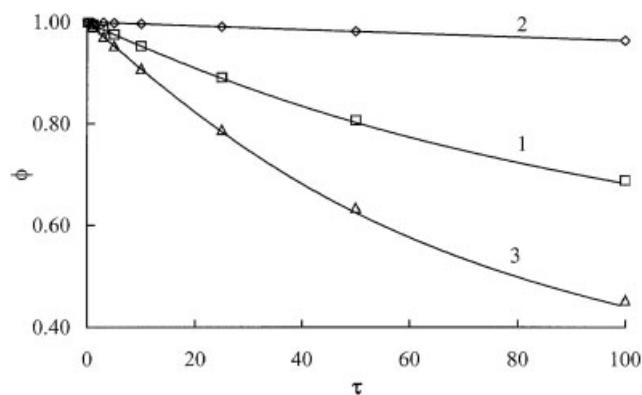


Figure 3 Dependence of the isotactic dyad fraction (ϕ) on the number of cleavages per average chain (τ). Theoretical calculations are shown by curves, and the Monte Carlo simulation is shown by points. The $k_{I1}/k_{I2}/k_{IS}/k_{S1}/k_{S2}$ rate constant ratios are (1) 1:1:1:1:1, (2) 1:0.04:0.2:0.04:1, and (3) 0.04:1:0.02:1:0.04. Initially, all chains consist of 100 units.

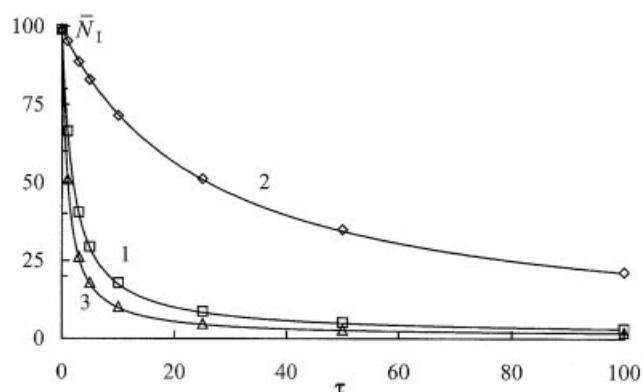


Figure 4 Average length of an isotactic sequence (\bar{N}_I) versus the number of cleavages per average chain (τ). The designations are shown in Figure 3.

$= 100$ (Fig. 5), most of the syndiosequences being formed by one to two dyads.

The agreement between the results of the numerical calculations and Monte Carlo simulation is excellent for ϕ and \bar{N}_I and satisfactory for \bar{N}_S . A little more intensive growth of syndiosequences in the Monte Carlo simulation might be attributed to the peculiarities of the algorithm. Indeed, the first step of the modeling consists in choosing two macromolecules. Because the molecular mass distribution rapidly converges to the Flory distribution, in which the number of chains rapidly falls with their polymerization degree, short chains undergo transesterification more often than they would if two dyads were directly chosen for the reaction. Accordingly, short chains contain most of the formed syndiodyads, which are more crowded and therefore form longer sequences. An improved algorithm for modeling transesterification will be presented elsewhere.

It may be concluded that in the course of transesterification, the reacting chains for a long time consist mainly of isosequences of decreasing length and contain short syndiosequences as configurational defects. Such a result may be practically important. For exam-

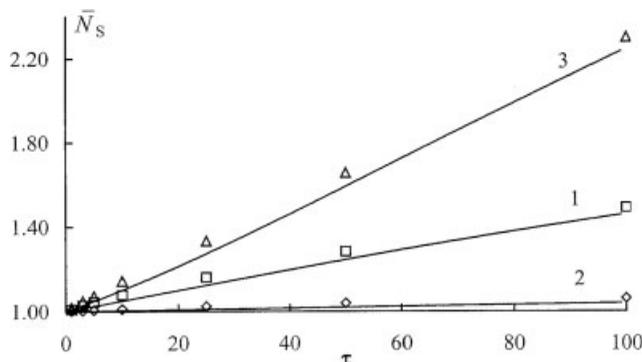


Figure 5 Average length of a syndiotactic sequence (\bar{N}_S) versus the number of cleavages per average chain (τ). The designations are shown in Figure 3.

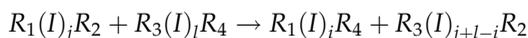
ple, if the initial polymer is crystallizable, then this property will be preserved during transesterification up to the high conversion degree. Then, it may appear impossible to follow the early stages of changing polymer stereoregularity during transesterification by NMR spectrometry because the concentration of syndiodyads and syndiotriads is small.

Thus, we have suggested the first theoretical model describing the evolution of polymer chain microtacticity in the course of transesterification. The model revealed some interesting features and was successfully tested by a Monte Carlo simulation.

APPENDIX: DETAILED KINETIC CONSIDERATIONS

Let m_{li} be the total number of sequences of i isodyads (i -sequences I). As shown in ref. 10, it is convenient to distinguish three types of i -sequences I: m_{1i} chains, m_{12i} end blocks, and m_{13i} internal blocks in chains containing both I and S dyads. Thus, the distribution of isosequences is determined by a set of variables, $\{m_{11i}, m_{12i}, m_{13i}\}$ ($i = 1 \dots \infty$), so that $m_{li} = m_{11i} + m_{12i} + m_{13i}$. A similar set, $\{m_{s1i}, m_{s2i}, m_{s3i}\}$, characterizes the distribution of syndiosequences over their length.

Now consider how the elementary reactions shown in Figure 1 influence the distribution of isosequences. The role of reaction $I + I \rightarrow I + I$ is almost equivalent to that of reaction $A-A$ when the evolution of the block length distribution in the course of the direct interchange is described:¹⁰



The only difference is that in the latter case the type of reacting unit remains unchanged, whereas two reacting I dyads yield either two I or two S dyads. Hence, the number of i -sequences I of type δ formed in a unit of time due to the reaction $I + I \rightarrow I + I$ may be written as follows:¹⁰

$$\sum_{\alpha, \beta=1}^3 \left(z k_{11} c_{\delta}^{(\alpha\beta)} / (4n) \right) \sum_{r=1}^i \sum_{j=r}^{\infty} \sum_{l=i-r+1}^{\infty} m_{1\alpha j} m_{1\beta l}$$

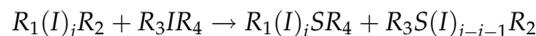
where

$$\hat{c}_1 = \begin{pmatrix} 2 & 1 & 0 \\ 1 & 1/2 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \hat{c}_2 = \begin{pmatrix} 0 & 1 & 2 \\ 1 & 1 & 1 \\ 2 & 1 & 0 \end{pmatrix},$$

$$\hat{c}_3 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1/2 & 1 \\ 0 & 1 & 2 \end{pmatrix}$$

n is the total number of dyads, and z is the average number of dyads with which a chosen dyad may react at the same moment of time.

As a result of reaction $I + I \rightarrow S + S$, an i -sequence I of type δ may appear after the cleavage of a longer ($j > i$) j -sequence I of type α ($\alpha = 1, 2$, or 3):



The number of such events per unit of time equals

$$\sum_{\alpha=1}^3 \left(z \phi k_{12} g_{\delta}^{(\alpha)} / 2 \right) \sum_{j=i+1}^{\infty} m_{1\alpha j}$$

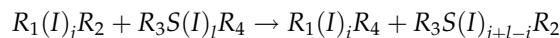
where

$$\hat{g} = \begin{pmatrix} 0 & 0 & 0 \\ 2 & 1 & 0 \\ 0 & 1 & 2 \end{pmatrix}$$

$\phi = \sum_{i=1}^{\infty} i m_{li} / n$ is the fraction of isodyads at the considered moment of time.

An elementary reaction, $I + S \rightarrow I + S$, is analogous to a reaction between A and B units in a blend of A and B polymers. Here several ways of forming an i -sequence I are possible. Let first a reacting dyad I belong to a j -sequence. Depending on the position of the dyad S that undergoes the reaction, one of the following situations (I–IV) is realized.

In case I, dyad S is a terminal dyad of l -sequence I ($l < i$):



In this case, i -sequences I ($i \geq 2$) are formed per unit of time in the amount of

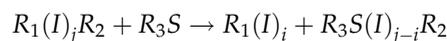
$$\sum_{\alpha, \beta=1}^3 \left(z k_{1S} d_{\delta}^{(\alpha\beta)} / (2n) \right) \sum_{l=1}^{i-1} \sum_{j=i-l}^{\infty} m_{1\alpha j} m_{1\beta l}$$

where

$$\hat{d}_1 = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \hat{d}_2 = \begin{pmatrix} 0 & 0 & 2 \\ 0 & 1/2 & 1 \\ 0 & 1 & 0 \end{pmatrix},$$

$$\hat{d}_3 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 2 \end{pmatrix}$$

In case II, dyad S is located at a chain end:



The rate of i -sequence formation due to the reaction (case II) is

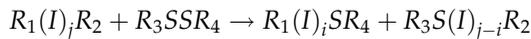
$$\sum_{\alpha=1}^3 \left(z k_{1S} f_{\delta}^{(\alpha)} / (2n) \right) m_{s\alpha} \sum_{j=i}^{\infty} m_{1\alpha j}$$

where

$$\hat{f} = \begin{pmatrix} 1 & 1/2 & 0 \\ 0 & 1/2 & 1 \\ 0 & 0 & 0 \end{pmatrix}$$

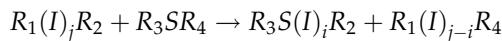
$m_{Se} = \sum_{i=1}^{\infty} (2m_{S1i} + m_{S2i})$ is the total number of end blocks S, and $f_{\delta}^{(\alpha)}$ depends on the type of the initial (α) and formed (δ) sequences I. Because the total number of chains (M) is constant, we can write $m_{Se} = 2M - 2m_{I1} - m_{I2}$, where $m_{I1} = \sum_{i=1}^{\infty} m_{I1i}$ and $m_{I2} = \sum_{i=1}^{\infty} m_{I2i}$ are the total numbers of isotactic chains and end blocks I, respectively.

In case III, dyad S is flanked by another dyad S:



Such a reaction yields $\sum_{\alpha=1}^3 (zk_{IS}g_{\delta}^{(\alpha)})/(2n) m_{SS} \times \sum_{j=i}^{\infty} m_{S\alpha j}$ i -sequences I of type δ per unit of time, where $m_{SS} = n(1 - \phi) - M + m_{I1} - m_{I3}$ is the total number of SS dyad pairs and $m_{I3} = \sum_{i=1}^{\infty} m_{I3i}$ is the total number of internal blocks I.

Note that in cases I-III, a reacting dyad S and a forming i -sequence I belong to different chains. The opposite situation (IV) is also possible when a dyad S after the reaction is situated at the boundary of a new-born i -sequence I:

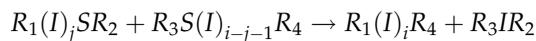


For that elementary reaction, the rate of i -sequence I formation equals

$$\sum_{\alpha=1}^3 (zk_{IS}g_{\delta}^{(\alpha)}(1 - \phi)/2) \sum_{j=i+1}^{\infty} m_{I\alpha j}$$

An elementary reaction, $S + S \rightarrow S + S$, does not lead to an appearance of new isosequences; therefore, we turn to another reaction, $S + S \rightarrow I + I$. Here also, several lines are possible:

In case V, both reacting dyads S are flanked by isosequences that finally are brought to one chain, thus forming an i -sequence I:



The number of such events per unit of time is

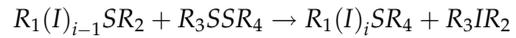
$$\sum_{\alpha, \beta=1}^3 (zk_{S2}h_{\delta}^{(\alpha\beta)})/(4n) \sum_{j=1}^{i-2} m_{I\alpha j} m_{I\beta i-j-1}$$

where

$$\hat{h}_1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \hat{h}_2 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix},$$

$$\hat{h}_3 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

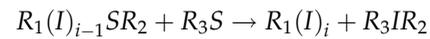
In case VI, one of the reacting dyads S borders on an $(i - 1)$ -sequence I, another one borders on a sequence S:



In the course of such a reaction, $\sum_{\alpha=1}^3 (zk_{S2}q_{\delta}^{(\alpha)})/(2n) \times m_{SS} m_{I\alpha i-1}$ i -sequences I of type δ are formed per unit of time, where

$$\hat{q} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

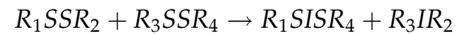
In case VII, dyad S neighbors with an $(i - 1)$ -sequence I, whereas another reacting dyad S is a terminal one:



It yields $\sum_{\alpha=1}^3 (zk_{S2}r_{\delta}^{(\alpha)})/(4n) m_{Se} m_{I\alpha i-1}$ new i -sequences I per unit of time, where

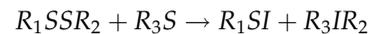
$$\hat{r} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 2 \\ 0 & 0 & 0 \end{pmatrix}$$

In case VIII, both reacting dyads S are flanked by syndiosequences:



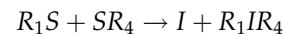
In that case, $zk_{S2}m_{SS}^2/(2n^2)$ internal ($\delta = 3$) isolated dyads I are formed per unit of time.

In case IX, one of the reacting dyads S borders on a syndiosequence, whereas another dyad is a terminal one:



Such a reaction results in the formation of $zk_{S2}m_{SS}m_{Se}/(2n^2)$ dyads I isolated at chain ends ($\delta = 2$).

In case X, both reacting dyads S are terminal:



It is found that $zk_{S2}m_{Se}^2/(8n^2)$ of isotactic dimers (chains of two units, $\delta = 1$) are formed per unit of time in that way.

Isosequences disappear because of the reactions of their constituent dyads I and the reactions, in which dyads S are involved that flank those sequences. In the first case, the number of I-sequences of length i and type δ decreases by $[\phi(k_{I1} + k_{I2})/2 + (1 - \phi)k_{IS}]im_{I\delta i}$ per unit of time, whereas in the second case this occurs by $(\phi k_{IS} + (1 - \phi)k_{S2})s_{\delta}m_{I\delta i}$, where the matrix $\hat{s} = (0,1/2,1)$.

Now it is possible to gather contributions of all considered situations in the kinetic equation describing the change in the number of i -sequences I of type δ in the course of transesterification:

$$\begin{aligned} \frac{1}{z} \frac{dm_{I\delta i}}{dt} = & \frac{k_{I1}}{4n} \sum_{\alpha, \beta=1}^3 c_{\delta}^{(\alpha\beta)} \sum_{r=1}^i \sum_{j=r}^{\infty} \sum_{l=i-r+1}^{\infty} m_{I\alpha j} m_{I\beta l} \\ & + \frac{k_{IS}}{2n} \sum_{\alpha, \beta=1}^3 d_{\delta}^{(\alpha\beta)} \sum_{l=1}^{i-1} \sum_{j=i-l}^{\infty} m_{I\alpha j} m_{I\beta l} + \frac{k_{IS} m_{Se}}{2n} \sum_{\alpha=1}^3 f_{\alpha}^{(\delta)} \sum_{j=1}^{\infty} m_{I\alpha j} \\ & + \frac{k_{IS} m_{SS}}{2n} \sum_{\alpha=1}^3 g_{\delta}^{(\alpha)} \sum_{j=i}^{\infty} m_{I\alpha j} + \frac{(k_{I2}\phi + k_{IS}(1-\phi))}{2} \\ & \times \sum_{\alpha=1}^3 g_{\delta}^{(\alpha)} \sum_{j=i+1}^{\infty} m_{I\alpha j} + \frac{k_{S2}}{4n} \sum_{\alpha, \beta=1}^3 h_{\delta}^{(\alpha\beta)} \sum_{j=1}^{i-2} m_{I\alpha j} m_{I\beta i-j-1} \\ & + k_{S2} \sum_{\alpha=1}^3 \lambda_{\delta}^{(\alpha)} m_{I\alpha i-1} + k_{S2} \delta_{i,1} a_{\delta} - ((k_{I1} + k_{I2})\phi/2 \\ & + k_{IS}(1-\phi))i + (k_{IS}\phi + k_{S2}(1-\phi))s_{\delta} m_{I\delta i}, \quad (A1) \end{aligned}$$

Matrices \hat{c} , \hat{d} , \hat{f} , \hat{g} , \hat{h} , and \hat{s} and quantities ϕ , m_{Se} , and m_{SS} have already been defined. $\delta_{i,1}$ is the Kronecker delta:

$$\begin{aligned} \hat{\lambda} = \frac{m_{SS}}{2} \hat{q} + \frac{m_{Se}}{4} \hat{r} = \frac{1}{n} \begin{pmatrix} 0 & m_{Se}/4 & 0 \\ 0 & m_{SS}/2 & m_{Se}/2 \\ 0 & 0 & m_{SS} \end{pmatrix} \\ \hat{a} = \frac{1}{2n^2} \begin{pmatrix} m_{Se}^2/4 \\ m_{Se} m_{SS} \\ m_{SS}^2 \end{pmatrix} \end{aligned}$$

To carry out the numerical solution of eq. (A.1), it is necessary to append the initial condition $m_{I\delta i}(t=0) = m_{I\delta i0}$ and specify the total numbers of chains and dyads. As soon as the dependence $m_{I\delta i}(t)$ is found, it

is possible to calculate the mass function of the block length distribution, $\Psi_{I\delta i} = im_{I\delta i}/\sum_{i,\delta} im_{I\delta i}$, which is equal to the probability for an arbitrarily chosen dyad I to belong to an i -sequence of type δ (isotactic chain or end block I or internal block I).

The distributions of I and S sequences change independently during the course of transesterification, just as the A and B block length distributions.¹⁰ Therefore, to get the kinetic equation for syndiosequences, it is just enough to replace ϕ by $1 - \phi$ and mutually change indices I and S in eq. (A.1).

Introducing now the total numbers of isodyads, $\phi = \sum_{i=1}^{\infty} im_{Ii}/n$, and iso- and syndiosequences, $m_I = \sum_{\delta=1}^3 \sum_{i=1}^{\infty} m_{I\delta i}$ and $m_S = \sum_{\delta=1}^3 \sum_{i=1}^{\infty} m_{S\delta i}$, respectively, we can reduce detailed eq. (A.1) by summations to more practically useful eqs. (1)–(3).

References

1. Transreactions in Condensation Polymers; Fakirov, S., Ed.; Wiley: Weinheim, 1999.
2. Litmanovich, A. D.; Platé, N. A.; Kudryavtsev, Y. V. *Prog Polym Sci* 2002, 27, 915.
3. Devaux, J.; Godard, P.; Mercier, J. P. *J Polym Sci Polym Phys Ed* 1982, 20, 1875.
4. Tessier, M.; Fradet, A. *e-Polymers* 2003, No. 030.
5. Benoit, H. C.; Fischer, E. W.; Zachmann, H. G. *Polymer* 1989, 30, 379.
6. McCullagh, C. M.; Blackwell, J.; Jamieson, A. M. *Macromolecules* 1997, 30, 4837.
7. Montaudo, M. S.; Montaudo, G.; Scamporino, E.; Vitalini, D. *Macromolecules* 1992, 25, 5099.
8. Beers, K. J.; Ray, W. H. *J Appl Polym Sci* 2001, 79, 246.
9. Kasperczyk, J. *Macromol Symp* 2001, 175, 19.
10. Kudryavtsev, Y. V.; Govorun, E. N. *e-Polymers* 2002, No. 033.
11. Platé, N. A.; Litmanovich, A. D.; Kudryavtsev, Y. V. *Polym Sci Ser A* 2004, 46, 1108.
12. Kudryavtsev, Y. V.; Govorun, E. N. *e-Polymers* 2003, No. 063.
13. Kudryavtsev, Y. V. *Macromol Theory Simul* 2000, 9, 675.
14. Jo, W. H.; Lee, J. W.; Lee, M. S.; Kim, C. Y. *J Polym Sci Part B: Polym Phys* 1996, 34, 725.
15. Jang, S. S.; Ha, W. S.; Jo, W. H.; Youk, J. H.; Kim, J. H.; Park, C. R. *J Polym Sci Part B: Polym Phys* 1998, 36, 1637.