

Is It Possible to Extend the Coleman–Fox Method for Polymer Sequence Determination by NMR to Copolycondensates?

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A new theory is presented for the interpretation of NMR spectra of copolycondensates, with special attention to those obtained by melt mixing of two macromolecular chains (reactive blending). The repeat unit is split into two parts, referred to as half-monomers. The present theory gives a highly accurate description of the changes in the sequence distribution during the reactive blending reaction, since the effect of the first and second neighbors along the macromolecular backbone (half-monomer penultimate effect) is explicitly considered. The theoretical predictions are compared with experimental data taken from the literature and, more specifically, NMR data concerning five copolymer systems, namely, a copolymer obtained by reactive blending of poly(ethylene terephthalate) and poly(ethylene adipate), an almost alternating copolymer with units of ether–sulfone and ether–ketone, a copolymer derived from 6-methyl-2,5-morpholinedione, and two copolymers obtained by reactive blending of poly(butylene terephthalate) with poly(bisphenolA carbonate) and Nylon6, respectively.

Introduction

Nuclear magnetic resonance (NMR) is a powerful analytical tool to analyze copolymers, and Coleman and Fox¹ developed a method for NMR usually referred to as the method of chain statistics. The method is now routine and Randall's book on polymer sequence determination using NMR discusses extensively the sequence information embedded in the NMR spectrum.² The method makes use of model sequence distributions, which are used to generate theoretical intensities. Thereafter, one compares them with the experimental ones. In some cases one uses best-fit minimization to find the parameters which define the model.^{3,4} Bovey suggested that two quantities are important, namely, the number of degrees of freedom, N_{freed} , which define the model, and the effective number of experimental points, N_{effexp} (effective number means that relations between data points are accounted for). Best-fit cannot be used for the systems which are underdetermined, that is, for systems in which N_{effexp} is smaller than N_{freed} , since the result is meaningless.⁵ The most popular sequence distribution models are the ultimate (also known as the terminal model) and the penultimate model. In the ultimate model, the probability of addition depends on the ultimate (terminal) unit of the growing chain. It can be shown that the sequence distribution is first-order markoffian (FOMA), which makes use of a probability matrix, the P-matrix for brief. In the penultimate model,⁶ the probability of addition depends on the penultimate unit of the growing chain as well as on the terminal unit. It can be shown that the sequence distribution is second-order markoffian (SEMA), in which eight numbers belong to a rectangular matrix, called the Q-matrix. The antepenultimate model (in which the rate of addition to the growing chain is affected by the incoming monomer, the terminal unit, as well as by the penultimate and the antepenultimate unit) was tentatively proposed, but nobody applied it. SEMA and FOMA share a very desirable property,

namely, they allow for recursion, in the sense that the abundance of sequences having length $(n + 1)$ and (n) are related together. In 1960, Miller and Nielsen⁷ used an important quantity for the characterization of their copolymers, namely, the degree of randomness (here it will be referred to as B_{ran}), defined as the sum of the elements which belong to the second diagonal of the P-matrix. When B_{ran} is close to zero, the copolymer has a strong alternating tendency and the heterodyads (AB) overwhelm the homodyads (AA and BB); when B is close to one, the copolymer is random (A and B are found at random along the chain); when B is almost two, the copolymer has long AAAAAA and BBBBBB blocks and the heterodyads are virtually absent. Other important quantities are the number-average length of long AAAAAA blocks, $\langle n_A \rangle$, the corresponding quantity for B, that is, $\langle n_B \rangle$ and the Ω -parameter, which grows as deviations from the behavior predicted by the terminal model grow and hence measures the strength of the penultimate effect⁸.

The Coleman–Fox method is tailored for addition copolymers, but for condensates the physical meaning of the P-matrix is lost. In fact, for free-radical processes the P-matrix measures the probability of adding monomer A or B to the growing chain. During the propagation stage, two growing chains cannot react with each other, otherwise bimolecular termination occurs and the growth stops. In the case of copolycondensates (especially those obtained by ester–ester and other exchange reactions) no monomer is present and the probability of adding monomer A or B cannot be easily defined. During the reaction, two chains react systematically with each other and the growth does not stop (it goes on). This problem was solved using the concept of an ideal chain. The probability matrix defines an ideal chain which has properties that resemble the sample's properties (composition, number-average lengths, abundance of dyads, abundance of triads, degree of randomness, etc.). The best probability matrix is the matrix which has properties that give the best-fit with experiment.

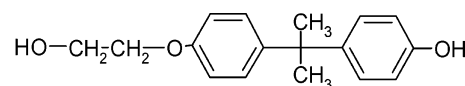
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Another problem remains unsolved. At a first sight, the NMR spectrum of a copolymer obtained by condensation looks perfectly similar to the NMR spectrum of a vinyl copolymer or a copolymer obtained by copolyaddition, since it displays dyads and triads (in some exceptional cases tetrads⁹ and even hexads¹⁰ are resolved). However, there are big differences, since dyads are pseudodyads and triads are pseudotriads. The difference is best explained with an example. Let's consider a copolymer obtained by reacting ethylene glycol (referred to as G), terephthalic acid (referred to as T) and succinic acid (referred to as S). The repeat units in the copolymer are GT and GS. In the following, the cited two parts of the repeat unit will be referred to as half-monomers. The NMR signals due to TGT, TGS, and SGS are usually referred to as triads (or G-centered triads). However, a triad should be made of three repeat units, and thus TGT is a set of three consecutive half-monomers. It is quite apparent that G, T, S cannot be found anywhere along the chain. Specifically, G cannot follow G, T cannot follow T, S cannot follow S, and T cannot follow S. Following the nomenclature used by our group,^{11–13} we shall refer to these forbidden combinations of half-monomers as sequence constraints.

In the case of spectra with four consecutive half-monomers, sequence constraints do not represent an obstacle and the extension of the Coleman–Fox method has been done, using a peculiar procedure, which will be referred to as the dual-row procedure (because each row of the P-matrix is determined independently) and, since it is important for our scope, it will be described in detail in the appendix. However, in general sequence constraints are difficult to account for, especially when copolycondensates are not formed by reacting small molecules but by other synthetic routes such as reacting together a homopolymer and a monomer or two homopolymers (by ester–ester and other exchange reactions). In our lab, we follow such reactions by taking aliquots at different times and recording both the NMR spectrum and the mass spectrum of the reaction products.^{14–16} These reactions have been addressed as transreactions and the subject has been reviewed.^{17,18} Several quantities have been introduced for the characterization of the copolymers formed, among which we find the unit block length¹⁹ and the h-degree.²⁰ During initial studies on transreactions,²¹ it was necessary to measure the extent of exchange, but this is not a polymerization reaction, the monomer-to-polymer yield is 100% initially and it remains 100% during the entire reaction. In order to overcome this difficulty, the quantity introduced by Miller and Nielsen (i.e., the degree of randomness) was proposed to describe the exchange yield. Fortunately, it was not necessary to scale (or rescale) B_{ran} , since it behaves exactly as a yield, namely, it is equal to zero at the beginning, it grows as the reaction proceeds, and it takes the value one (i.e., 100%) when the reaction has gone to completion. Despite this lucky circumstance, the task of modeling the changes in the sequence during melt mixing of homopolymers remains very complex. For instance, let us consider a copolymer obtained reacting G with S, then reacting G with T, and then letting the homopolymers react. In other words, a copolymer obtained melt-mixing poly(ethylene succinate) with poly(ethylene terephthalate). In the initial stages, picking up at random three consecutive half-monomers, the first two being SG, there is a very high probability that the three consecutive half-monomers are SGS and a very low probability that the three consecutive half-monomers are SGT. Following the nomenclature used in free-radical penultimate effect copolymerization (since G is the terminal half-monomer and since the distance between the initial

and the final half-monomer in SGS and SGT is three), there is a strong penultimate half-monomer effect. To the best of my knowledge, this additional difficulty has never been accounted for, most probably for the following reason. In copolymer obtained by condensation, the difference $N_{\text{effexp}} - N_{\text{freed}}$ comes usually very close to Bovey's limit (see above), the number of points (NMR peaks) is limited, and models which possess a large N_{freed} cannot be employed. Hence, it is not surprising that sequence distribution models expressly developed for copolymers obtained by condensation do not account for this effect.

Copolycondensates have been approached from a theoretical point of view and Marechal and Fradet²² reviewed the field up to 1989. Vasnev and Kuchanov²³ introduced a microheterogeneity index, K_M , and they calculated its values as a function of the reactivity of the functional groups present in the reaction mixture. They noted that the abundance of dyads and triads are related, and they reported pertinent relationships. They also introduced an orientation coefficient, which is claimed to be useful in the case of diols of the type



Unfortunately, they adopted a cumbersome notation, with arrows to indicate the orientation of the diol. The theory by Lopez-Serrano et al.²⁴ predicts the sequence distribution of the copolymer, but it lacks sufficient generality since it includes the case of a copolymer of three components (e.g., a diol and two diacids or alternatively a diacid and two diols) but it does not include relatively common cases such as the case of four components (i.e., two diols and two diacids) or complex cases (e.g., three diols and/or three diacids). On the other hand, the method by Zetterlund et al.^{25,26} can deal with complex cases. Furthermore, it is able to take into account different reactivities to predict the microstructure of the chain and it lends itself to a very detailed comparison with experiment. It also allows one to predict the time development of the sequence distribution, but it makes use of Monte Carlo methods, which have small uncertainties, and therefore it may be difficult to perform a minimization on the parameters of the model. The theory by Beer and Ray²⁷ requires the knowledge of the rate constants of polymerizations, which are sometimes unavailable.

The Coleman–Fox method of selecting a model sequence distribution, generating a theoretical NMR spectrum, and comparing it with the experimental one is straightforward but tedious, and some authors felt the need for some simple formulas to estimate the degree of randomness and the number-average lengths of like monomers $\langle n_A \rangle$ and $\langle n_B \rangle$. These simple formulas are based on a linear combination of NMR intensities of dyads and/or triads in the spectrum, and they will be referred to as stoichiometric relationships. In a series of four consecutive papers concerning the reaction products obtained when mixing and heating poly(butylene terephthalate) together with poly(bisphenol A carbonate), Devaux et al.²⁸ in 1982 developed a theory for the interpretation of NMR spectra of copolymers which makes use of half-monomers and stoichiometric relationships. The theory enjoyed enormous success, and it was used for the interpretation of NMR spectra of a number of other copolymers obtained by condensation^{29–38} such as esters, carbonates, nylons, and ethers. Recently, Tessier and Fradet published a theoretical account which deals with unsymmetrical monomers with particular emphasis on the case in which one of the homopolymers is obtained by condensing a diol with a diacid and the other one is obtained from a lactone.³⁹ However,

stoichiometric relationships yield only gross estimates for copolymer composition, B_{ran} , $\langle n_A \rangle$ and $\langle n_B \rangle$, since they make use of approximations. The copolymer composition derived from dyads intensities differs from the composition derived from triads intensities, and both values are affected by error (since the composition is defined as a summation over all sequences and thus both dyads and triads intensities contribute to the final result). In a similar manner, the number-average length derived from dyads intensities is only a gross estimate since $\langle n_A \rangle$ and $\langle n_B \rangle$ are defined as the ratio between two summations (both over all sequences, but with different weights). The use of stoichiometric relationships causes a loss of information. The error introduced spoils the experimental effort which consists of recording the NMR spectrum and performing peak assignment (this operation is time consuming since it often requires one to synthesize model compounds and model polymers, to record their NMR spectra, and to compare them with the NMR spectrum of the sample). The method which uses stoichiometric relationships is inadequate because it is inefficient, and the main cause for this is that it assumes that half-monomers follow the FOMA model. This approximation is unsatisfactory. Therefore, a better theory (which does not suffer of this drawback, since it relies on a more flexible model, i.e., the SEMA model) is developed here.

The new model is described in the Theoretical Section. Thereafter, the theoretical predictions are compared with experimental data taken from the literature, and it will be shown that more information can be “squeezed” from the experimental data. More specifically, the new theory is highly efficient and it is able to extract all the information on the copolymer sequence contained in the NMR spectrum.

Theoretical Section

In this section a new theory is developed, which is able to take into account penultimate effects and to model the changes in the NMR spectrum as the exchange reaction (i.e., the transreaction) proceeds. Let's consider the case of a copolymer which possesses a repeat unit which can be split into two half-monomers, say A and C and another repeat unit which can be split into two half-monomers, B and C. Copolymers of this type are formed during the reactive blending of two relatively similar homopolymers, in the sense that they have a half-monomer in common (referred to as C). In order to describe the sequence distribution of the copolymer, a matrix is introduced, and it will be referred to as the Q-matrix. It has 27 elements, namely, Q_{AAA} , Q_{AAB} , Q_{AAC} , Q_{BAA} , Q_{BAB} , Q_{BAC} , Q_{CAA} , Q_{CAB} , Q_{CAC} , Q_{ABA} , Q_{ABB} , Q_{ABC} , Q_{BBA} , Q_{BBB} , Q_{BBC} , Q_{CBA} , Q_{CBB} , Q_{CBC} , Q_{ACA} , Q_{ACB} , Q_{ACC} , Q_{BCA} , Q_{BCB} , Q_{BCC} , Q_{CCA} , Q_{CCB} , Q_{CCC} . One may have the impression that N_{freed} is very large, but this is not true, as shown in the following. Obviously A, B, and C cannot be found anywhere along the chain. In other contexts, forbidden combinations of half-monomers have been considered and they were referred to as sequence constraints. Specifically AB, BA, AA, BB, and CC are forbidden and some Q-matrix elements are zero, namely, Q_{AAA} , Q_{AAB} , Q_{AAC} , Q_{BAA} , Q_{BAB} , Q_{BAC} , Q_{CAA} , Q_{CAB} , Q_{ABA} , Q_{ABB} , Q_{ABC} , Q_{BBA} , Q_{BBB} , Q_{BBC} , Q_{CBA} , Q_{CBB} , Q_{ACC} , Q_{BCC} , Q_{CCA} , Q_{CCB} , Q_{CCC} . In this way $N_{\text{freed}} = 6$. Some of the Q-matrix elements are related together by simple relationships, usually referred to (especially in textbooks) as normalization conditions, that is

$$Q_{CAC} = 1, \quad Q_{CBC} = 1 \quad (1a)$$

$$Q_{ACA} + Q_{ACB} = 1, \quad Q_{BCA} + Q_{BCB} = 1 \quad (1b)$$

Eventually, $N_{\text{freed}} = 2$, and this represents a good result, since a two-parameter model is very appealing. As cited in the Introduction, a very desirable property is the recursive one, in the sense that the abundance of sequences having length $(n + 1)$ and (n) are related together. In the SEMA model, the molar fraction, I_{XXWYZ} , of oligomers with sequence XXWYZ is obtained from shorter oligomers using the following recurrence formula

$$I_{XXWYZ} = I_{XXWY}Q_{WYZ} \quad (2)$$

where X, W, Y, and Z belong to the set {A, B, C}. When the length of the sequence (λ) is smaller than three, this formula becomes $I_X = c_X$ (valid for $\lambda = 1$) or $I_{XX} = c_X \rho_{XX}$ (valid for $\lambda = 2$), where c_X is the composition (i.e., the molar fraction of X units) associated with the Q-matrix and ρ_{XX} is an element of a smaller (3×3) matrix associated with the Q-matrix. Using recurrence, a combination of Q-matrix elements is obtained. For instance, the molar fraction of oligomers having sequence ACBCACB is given by

$$I_{ACBCACB} = c_A \rho_{AC} h_1 \quad (3)$$

where $h_1 = Q_{ACB} Q_{CBC} Q_{BCA} Q_{CAC} Q_{ACB}$. Using the above equations, one can generate a theoretical NMR spectrum and compare it directly with the experimental one. It is also possible to generate the mass spectra, but that is beyond the scope of this paper.

Important quantities for the characterization of the copolymer are the degree of randomness and the Ω -parameter. The degree of randomness is the sum of the elements which belong to the second diagonal of the ρ -matrix:

$$B_{\text{ran}} = \rho_{CA} + \rho_{AC} \quad (4)$$

Randall (in his book on polymer sequence determination) discusses the number-average length of long AAAAAA blocks, $\langle n_A \rangle$. One considers the abundances (denoted as I_ϵ) of sequences of the type $Z(A)_\epsilon Z$, where Z is B or C. The averaging process is accomplished by taking the number average of I_ϵ (the index ϵ ranges from zero to infinity). In the FOMA model, $\langle n_A \rangle$ is given by $(1 - P_{AA})^{-1}$ (see any textbook or see the Appendix). In the case of sequence constraints, $\langle n_A \rangle$ is useless (it always takes the same value) and a different quantity must be introduced, namely, the number-average length of long ACA-CACAC blocks, $\langle n_{AC} \rangle$. One considers the abundances (denoted as I_ϵ) of sequences of the type $BC(AC)_\epsilon B$. By definition, the number average, $\langle n_{AC} \rangle$ is the ratio between γ_1 (the sum of ϵI_ϵ) and γ_0 (the sum of I_ϵ). In our case, γ_0 equals $(1 - Q_{CAC}Q_{ACA})^{-2}$ (it is a modified geometric series with argument $Q_{CAC}Q_{ACA}$), whereas γ_1 is a regular geometric series. However, $Q_{CAC} = 1$ and thus

$$\langle n_{AC} \rangle = (1 - Q_{ACA})^{-1} \quad (5)$$

The Ω -parameter measures the strength of the penultimate effect. It is given by the ratio between two polynomials of the fourth order in c_A (the molar fraction of A). The fourth order is reached as $(3 + 1)$ in the numerator and as $(2 + 2)$ in the denominator. In our case Ω is given by $c_A Q_{AAA} / \rho_{AA} \rho_{AA}$, which is clearly useless, since A cannot follow A. An interesting alternative is to define the Ω -parameter as $c_A Q_{ABA} / \rho_{AB} \rho_{BA}$.

The case in which the two homopolymers are so similar that they have a half-monomer in common is relatively simple. Unfortunately, in many melt-mixing reactions, the two homopolymers are not similar and they do not have a half-monomer

in common. Let's consider the case of a copolymer which possesses a repeat unit which can be split into two half-monomers, say A and B and another repeat unit which can be split into two half-monomers, C and D. A probability matrix is introduced, and it will be referred to as the L-matrix. It possesses 64 elements, namely, $L_{AAA}, L_{AAB}, L_{AAC}, L_{AAD}, L_{BAA}, L_{BAB}, L_{BAC}, L_{BAD}, L_{CAA}, L_{CAB}, L_{CAC}, L_{CAD}, L_{DAA}, L_{DAB}, L_{DAC}, L_{DAD}, L_{ABA}, L_{ABB}, L_{ABC}, L_{ABD}, L_{BBA}, L_{BBB}, L_{BBC}, L_{BBB}, L_{CBA}, L_{CBB}, L_{CBC}, L_{CBD}, L_{DBA}, L_{DBB}, L_{DBC}, L_{DBD}, L_{ACA}, L_{ACB}, L_{ACC}, L_{ACD}, L_{BCA}, L_{BCB}, L_{BCD}, L_{CCA}, L_{CCB}, L_{CCC}, L_{CCD}, L_{DCA}, L_{DCB}, L_{DCC}, L_{DCD}, L_{ADA}, L_{ADB}, L_{ADC}, L_{ADD}, L_{BDA}, L_{BDB}, L_{BDC}, L_{BDD}, L_{CDA}, L_{CDB}, L_{CDC}, L_{CDD}, L_{DDA}, L_{ddb}, L_{DDC}, L_{DDD}$. In our case, AC, CA, BD, DB, AA, BB, CC, DD are forbidden and therefore 48 L-matrix elements are zero (their identification is omitted for brevity). Thus, $N_{\text{freed}} = 64 - 48 = 16$. Some of the L-matrix elements are related together by the following relationships

$$L_{ABA} + L_{ABC} = 1, \quad L_{ADA} + L_{ADC} = 1 \quad (6a)$$

$$L_{BAB} + L_{BAD} = 1, \quad L_{BCB} + L_{BCD} = 1 \quad (6b)$$

$$L_{CBA} + L_{CBC} = 1, \quad L_{CDA} + L_{CDC} = 1 \quad (6c)$$

$$L_{DAB} + L_{DAD} = 1, \quad L_{DCB} + L_{DCD} = 1 \quad (6d)$$

In this way, $N_{\text{freed}} = 16 - 8 = 8$. In the particular case of copolymers formed by reacting together two homopolymers, some further simplification occurs. Chains with AD or BC appear in the reaction mixture only at long reaction times, when long ABABABAB and CDCDCDCD sequences are no longer present. In these chains, penultimate effects are negligibly small. As a result:

$$L_{ADA} = L_{ADC}, \quad L_{BCB} = L_{BCD} \quad (7a)$$

$$L_{DAB} = L_{DAD}, \quad L_{CBC} = L_{CBA} \quad (7b)$$

Thus, $N_{\text{freed}} = 8 - 4 = 4$. Using $L_{ABA}, L_{BAB}, L_{DAB}$, and L_{CBC} , the sixteen L-matrix elements of interest are found and the molar fraction, I_{XXWYZ} , of oligomers with sequence XXWYZ is obtained from shorter oligomers using following the recurrence formula

$$I_{XXWYZ} = I_{XXWY}L_{WYZ} \quad (8)$$

where X, W, Y, and Z this time belong to another set, namely, {A, B, C, D}. When the length of the sequence (λ) is smaller than three, this formula becomes $I_X = c_X$ (valid for $\lambda = 1$) or $I_{XX} = c_X \nu_{XX}$ (valid for $\lambda = 2$), where c_X is the composition (molar fraction of X units) associated with the L-matrix and ν_{XX} is an element of a smaller (4×4) matrix associated with the L-matrix. Using recurrence, a combination of L-matrix elements is obtained. For instance, the molar fraction of oligomers having sequence DCBADBC is given by

$$I_{DCBADBC} = c_D \nu_{DC} h_2 \quad (9)$$

where $h_2 = L_{DCB}L_{CBA}L_{BAD}L_{ADB}L_{DBC}$. The sum of the elements which belong to the second diagonal of the ν -matrix gives the degree of randomness

$$B_{\text{ran}} = \nu_{DA} + \nu_{CB} + \nu_{BC} + \nu_{AD} \quad (10)$$

By analogy with terpolymers, it is useful to introduce the number-average length of long CDCDCDCD sequences, re-

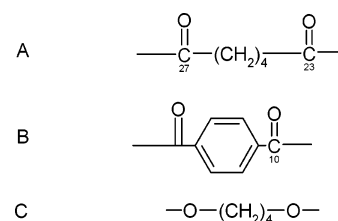
ferred to as $\langle n_{CD} \rangle$. One considers the abundances (denoted as I_e) of sequences of the type B(CD)_nA. By definition, $\langle n_{CD} \rangle$ is the ratio between γ_4 (the sum of I_e) and γ_3 (the sum of I_e). In our model, γ_4 equals $(1 - L_{CDC}L_{DCD})^{-2}$, whereas γ_3 is given by $(1 - L_{CDC}L_{DCD})^{-1}$. Simplifying

$$\langle n_{CD} \rangle = (1 - L_{CDC}L_{DCD})^{-1} \quad (11)$$

Equations 1–11 constitute a model which is able to accurately describe the sequence of copolymers obtained by melt mixing because the effect of the penultimate unit is taken into account. The above equations were implemented in a computer program called NACCOS (NMR analysis of copolymers by constrained second-order markoffian). It accepts as input the intensities of the NMR spectrum, the half-monomers along with the sequence constraints, and it computes the degree of randomness, the number-average lengths, and it generates the theoretical NMR spectrum. It also finds the best Q-matrix or the best L-matrix, depending on whether the two homopolymers possess a half-monomer in common or not. The spectrum is generated at (almost) infinite resolution. There is a plan to add a distinct section which degrades the resolution using Lorentian line shapes to allow for deconvolution.^{40,41} No attempt was made to predict the chemical shift for each sequence.

Results and Discussion

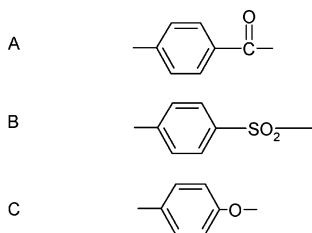
A test of the newly developed method was performed using NMR data concerning copolycondensates, which appeared in the literature. Poly(ethylene adipate) was mixed with poly(ethylene terephthalate),¹⁴ the two polymers were closed in a sealed tube and melt mixed at 290 °C. The three half-monomers A, B, and C, are



The copolymer mixed for 20 min will be referred to as sample M20. It is expected to possess a large degree of "blockiness" and thus to display a strong penultimate half-monomer effect (since the heating time is short). The proton NMR spectrum of sample M20 shows three peaks in the region of 4–5 ppm due to the C-centered triads, namely, ACA, ACB, and BCB. The experimental peak intensities were given as input to the computer program NACCOS, eq 2 was used to generate theoretical intensities, and the result was $Q_{ACA} = 0.565$, $Q_{BCB} = 0.900$. Starting from these values, the number-average lengths (see eq 5) were computed, and the values were $\langle n_{AC} \rangle = 2.3$, $\langle n_{BC} \rangle = 10$. The number-average values obtained by the Q-matrix approach are identical with the values obtained by the dual-row method.¹⁴ This implies that the new method gives the correct answer.

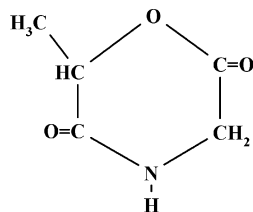
Some years ago, a series of copolymers with units of ether–sulfone and ether–ketone were obtained.¹⁰ Sample S4 is almost alternating since it was obtained by reacting 4-4'-difluorobenzophenone with bis(4-hydroxyphenyl)sulfone in 1:1 molar ratio. Experimental data demonstrated that some rearrangements occurred, and thus the copolymer possesses a small amount of

sequences which are incompatible with an exactly alternating structure. The three half-monomers A, B, and C, are

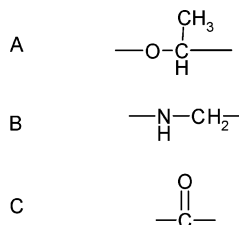


The strong alternating tendency causes a penultimate effect, and this is surely expected not to be negligible. In fact, picking up at random three consecutive half-monomers, the first two being AC, there is a very high probability that the three consecutive half-monomers are ACA and a very low probability that the three consecutive half-monomers are ACB. The carbon NMR spectrum of sample S4 shows four peaks in the region of 118–120 ppm and seven peaks in the region of 132–137 ppm. The 11 experimental peak intensities were given as input to the computer program NACCOS, and eq 2 was used to generate theoretical intensities. The best-fit minimization converged quickly toward the following result: $Q_{ACA} = 0.338$, $Q_{BCB} = 0.096$. This implies that A units are slightly more abundant than B units, the A/B molar ratio being 57/43. The number-average lengths (see eq 5) were computed, and the values were $\langle n_{AC} \rangle = 1.5$, $\langle n_{BC} \rangle = 1.1$. This implies that there are deviations from a perfectly alternating copolymer ($\langle n_{AC} \rangle = \langle n_{BC} \rangle = 1$), the ACACAC sequences being abundant and the BCBCBC sequences being rare. These findings are in excellent agreement with experimental evidence¹⁰ (obtained by mass spectrometry), and this implies that the new method is highly reliable.

A series of copolymers were synthesized by ring-opening copolymerization starting from 6-methyl-2,5-morpholine-dione^{42,43} (referred to as CycGL)



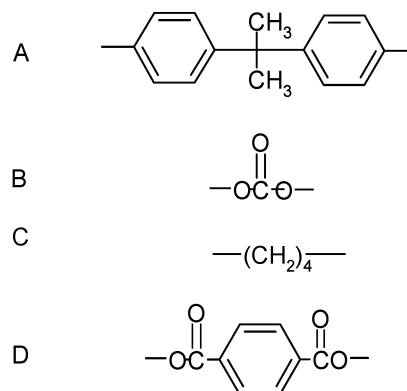
and the lactic acid cyclic dimer (referred to as CycLL). Sample T11 was obtained by reacting the two cyclic dimers in 1:1 molar ratio.⁴³ The three half-monomers A, B, and C, are



The ¹H NMR spectrum of sample T11 has been reported.⁴³ The doublet at 1.58 and 1.54 ppm is due to ACACA, whereas the doublet at 1.51 and 1.48 ppm is due to ACACB. Due to the peculiar structure of CycGL, the BCBC sequence is forbidden. This introduces a major simplification, since it can be shown that $Q_{BCB} = 0$ (the computation is straightforward: imposing that $I_{BCBC} = 0$, bearing in mind that $I_{BCBC} = c_B \rho_{BC} Q_{BCB} Q_{CBC}$, it follows that $Q_{BCB} = 0$). In practice, for this particular system,

$N_{\text{free}} = 1$ and, starting from a single Q-matrix element (i.e., Q_{ACA}), one can reconstruct the remaining 20 elements. This represents an unexpected result since it is possible to generate theoretical NMR intensities using a single parameter. Nevertheless, two questions remain, namely, if BCACB sequences should be present in sample T11 and if they are significantly present. In order to shed some light on this subject, the computer program NACCOS was used to predict the theoretical NMR intensities of A-centered pentads for sample T11, and the result was $I_{ACACA}/I_{ACACB}/I_{BCACB} = 57/29/14$. In practice, a small amount of BCACB sequences should be present. The second question cannot be answered by a calculation. However, a note is in place. The NMR spectrum of sample T11 displays a weak structure around 2 ppm. If the structure is assigned to BCACB, the experimental NMR intensities of A-centered pentads become 58/30/12, and these values are reasonably close to 57/29/14.

As discussed above, the case in which the two homopolymers have a half-monomer in common is relatively simple. Unfortunately, in many melt-mixing reactions, the two homopolymers are more complex. Devaux et al.²⁸ studied the reactive blending of poly(butylene terephthalate) (PBT for brief) and poly(bisphenolA carbonate) (PC for brief) at 290 °C. The four half-monomers A, B, C, and D are



Sample S15 is reacted for 15 min, whereas sample S31 is reacted for 31 min. The heating time is short, and the abundance of homosequences in the two samples is expected to be high. In other words the two samples should display a strong penultimate half-monomer effect which reflects the large degree of “blockiness”. The ¹³C NMR spectra of S15 and S31 displayed a series of peaks in the region of 60–160 ppm, the most notable peaks at 66–69, 119–120, 128–130, and 147–148 ppm.

Table 1 reports NMR data for the S31 copolymer. In the first column are the chemical shifts in ppm. In the second column are the NMR experimental intensities. The method based on stoichiometric relationships was applied to sample S31 (the number-average length of butylene terephthalate), and the result was $\langle n_{CD} \rangle = 6.9$. This result is not satisfactory, since it is affected by error. In order to show that better sequence information can be extracted from the experimental data, the seventeen experimental peak intensities for sample S31 were given as input to the computer program NACCOS and eq 8 was used to generate theoretical intensities. The best-fit minimization converged and Table 1 column 3 reports the theoretical NMR intensities at the minimum. It can be seen that the experimental and theoretical NMR intensities agree very well, which proves the power of the novel method. The parameters which gave the best-fit were $L_{ABA} = 0.322$, $L_{BAB} = 0.305$, $L_{DAB} = 0.095$, and $L_{CBC} = 0.111$. From these values, the 16 nonvanishing L-matrix elements were reconstructed using eqs 6 and 7. In particular $L_{DCD} = 0.205$, $L_{DCD} = 0.147$, and

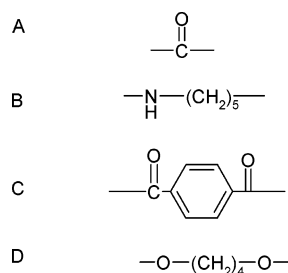
TABLE 1: Experimental NMR Data for Sample S31 (PC/PBT Copolymer) Taken from the Literature²⁷ along with Theoretical NMR Intensities Computed Using the New Model

shift ^a	experimental ^b	theoretical ^c
65.7	26	28
68.1	0	1
68.7	5	4
168.3	29	28
167.5	3	4
132.3	3	4
132.9	27	26
133.4	3	4
128.9	86	87
129.6	15	14
154.8	6	6
155.8	4	4
156.3	0	0
147.7	19	21
147.3	6	4
119.1	59	60
119.6	19	18

^a Chemical shift from TMS (in ppm). ^b Experimental NMR intensities for sample S31 taken from the literature.²⁷ ^c Theoretical NMR intensities for sample S31 computed using NACCOS.

these values were inserted in eq 11. The resulting value was $\langle n_{CD} \rangle = 10.3$. This value is different from that obtained by Devaux et al.²⁸ (namely, 6.9, see above), and this implies that the two methods for extracting sequence information are not equivalent. Clearly, the new method is more efficient since it is not affected by error. Data for sample S15 were not processed, since it is known that experimental intensities are not very reproducible, due to preheating before melt mixing. This shortcoming can be avoided. The melt mixing of PC and PBT was studied also in our lab,⁴⁴ but the apparatus allows one to study reaction times as short as 2, 4, 6, 8, and 10 min.

The new model can easily handle simple cases in which the penultimate half-monomer effect is very weak or absent. Recently, our group studied the reactive blending of Nylon6 with poly(butylene terephthalate).¹⁵ The melt mixing was carried at 260, 270, and 280 °C. The four half-monomers A, B, C, and D are



Sample C28 is melt mixed at 280 °C for 60 min, and at these time and temperature conditions, the exchange reaction should be at the final stages. For this reason, long ABABAB and CDCDCD sequences are expected to be systematically absent, and the penultimate half-monomer effect should disappear in the sense that picking up at random three consecutive half-monomers, the first two being AB, the probability that the three consecutive half-monomers are ABA or ABC are (approximately) the same. The ¹³C NMR spectrum of sample C28 displays peaks at 165–175 ppm due to C=O, 129–131 ppm due to aromatic carbons, 65–67 ppm due to butylene carbons, 23–29 ppm due to aliphatic carbons (mainly nylon carbons along with some butylene carbons), and 177–179 ppm due to

TABLE 2: Experimental NMR Data for Sample C28 (Ny6-PBT Copolymer) Taken from the Literature¹⁵ along with Theoretical NMR Intensities Computed Using the New Model

chemical shift ppm ^a	experimental ^b	theoretical ^c
24.2	13	14
24.3	28	28
25.1	26	24
25.2	68	70
25.8	8	8
26.0	22	22
26.15	8	8
65.7	16	15
66.47	42	43
129.4	13	13
129.7	3	4
130.14	53	54
130.67	16	14
167.8	15	14
168.3	43	44
172.4	4	5
172.92	11	10
177.83	13	12
178.28	12	13

^a Chemical shift from TMS (in ppm). ^b Experimental NMR intensities for sample C28 taken from the literature.¹⁵ ^c Theoretical NMR intensities for sample C28 computed using NACCOS.

aliphatic carbon bonded to a carbonyl.¹⁵ Table 2 reports NMR data for the Ny6/PBT copolymer. The first and the second columns report the chemical shift of NMR peaks and experimental intensities, respectively. The 19 experimental peak intensities for sample C28 were given as input to the computer program NACCOS and eq 8 was used to generate theoretical intensities. The iterative procedure compared experimental and theoretical intensities. The best-fit converged and Table 2 column 3 reports the theoretical NMR intensities at the minimum. From inspection it can be seen that there is a close match. The parameters which gave the best-fit were $L_{ABA} = 0.611$, $L_{BAB} = 0.854$, $L_{DAB} = 0.588$, and $L_{CBC} = 0.621$. Thereafter eqs 6 and 7 yielded the other 16 nonvanishing L-matrix elements. In particular $L_{DCD} = 0.708$, $L_{DCD} = 0.722$, and thus (see eq 11) the number-average length for butylene terephthalate is $\langle n_{CD} \rangle = 2.1$. This value is very close to the value 2, which characterizes a completely random chain, and it is not too far from the value obtained by mass spectrometry¹⁵ (i.e., $\langle n_{CD} \rangle = 1.7$). In practice, the result obtained is compatible with the kinetics of the blending reaction, it agrees with other experiments, and it thus demonstrates that the new method is effective.

Conclusions

The extension of the Coleman–Fox method for polymer sequence determination by NMR to copolycondensates is indeed possible. The new theory was tested in various situations, and it turned out to be reliable. It is particularly useful for samples obtained by melt mixing of two macromolecular chains (reactive blending).

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Appendix

In this appendix, the dual-row procedure is described. The procedure was initially developed for free-radical copolymers, and it applies when there are three different half-monomers (one

is in common, i.e., the two homopolymers share one half-monomer) and triads are presents in the NMR spectrum. Joining the first and the third half-monomers together, one obtains one of two repeat units, namely, α , whereas joining the first and the second one together, one obtains the other repeat unit, namely, β . Four numbers $P_{\alpha\alpha}$, $P_{\alpha\beta}$, $P_{\beta\alpha}$, and $P_{\beta\beta}$, are grouped together in a 2×2 matrix, called the P-matrix. The molar fraction of $\alpha\alpha$ and $\beta\beta$ sequences ($I_{\alpha\alpha}$ and $I_{\beta\beta}$), are given by

$$I_{\alpha\alpha} = c_{\alpha}P_{\alpha\alpha}, \quad I_{\beta\beta} = c_{\beta}P_{\beta\beta} \quad (\text{A1})$$

where c_{α} and c_{β} are the molar fractions of A and B units. This system can be solved (note that N_{effexp} equals N_{freed}) and the P-matrix is given by

$$P_{\alpha\alpha} = I_{\alpha\alpha}/c_{\alpha}, \quad P_{\beta\beta} = I_{\beta\beta}/c_{\beta} \quad (\text{A2})$$

The number averages are easily derived using the following relationship

$$\langle n_{\alpha} \rangle = (1 - P_{\alpha\alpha})^{-1}, \quad \langle n_{\beta} \rangle = (1 - P_{\beta\beta})^{-1} \quad (\text{A3})$$

The usefulness and the simplicity of the dual-row procedure are quite apparent.

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