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Characterization of a Polymeric Chain by Pyrolysis Gas Chromatography and Computer Simulation

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ABSTRACT: A method has been developed which utilizes the experimental results from pyrolysis−gas chromatography (Py−GC) integrated with that from a Monte Carlo simulation to characterize the microstructure of a copolymer chain. The bridge between Py−GC and the Monte Carlo simulation is the relative triad peak intensities as well as the “number-average sequence length” values. By appropriate adjustment of the copolymerization parameters such as relative reactivity ratio, the triad intensity profile from a Monte Carlo simulation can be successfully fit to the Py−GC experimental values of relative trimer intensities. If the triad intensity profile and the value of “number-average sequence length” are a unique parameter set for every copolymer chain microstructure, all copolymer microstructure information on the real polymer can be explored based on the chain created by the Monte Carlo simulation. The development of this method makes it possible to extend microstructure determination beyond the current instrumentation limit.

Introduction

A complete understanding of the monomer arrangement in a polymeric chain is always the ultimate goal in copolymer microstructure characterization. The most effective and efficient way to achieve this purpose is to count and examine each monomer from the beginning to the end of a polymeric chain. Unfortunately, there is neither a microscopic nor spectroscopic technique at the current time capable of accomplishing this task. Since direct measurement is not possible, there are several indirect ways that have been developed in recent years to describe the monomer distribution in a copolymer chain.[1,2]

One of the common approaches to describe the monomer arrangement in the copolymer chain is called “number-average sequence length”. The “number-average sequence length” of a monomer A in an A−B copolymer chain can be defined as n_A, where n_A equals the total number of “A monomers” in the polymer chain divided by the total number of blocks of “monomer A”. The formula can be expressed as

$$n_{\mathrm{A}} = \frac{\text{total number of A}}{\text{total blocks of A}}$$

This definition and the formula associated with it have been used for polymer chain characterization for a long time.[3]

The “number-average sequence length” calculation is based on the triad abundance of a copolymer. Consider the A−B copolymer as an example. There are eight possible combination of triads. They are pure A triad (labeled AAA), the triad of two A and one B (labeled AAB, BAA, and ABA), the triad of one A and two B (labeled BBA, ABB, and BAB), and the pure B triad (labeled BBB). The total number of A monomer can be expressed with A-centered triad terms as AAA + (AAB + BAA) + BAB. The total number of blocks of A monomer can be expressed with A centered triad terms as ($^1/_2$) (AAB + BAA) + BAB.[4] The “number-average sequence length” formula can be obtained based on the triad terms as follows:

$$n_{\mathrm{A}} = \frac{n_{\mathrm{AAA}} + n_{\mathrm{AAB+BAA}} + n_{\mathrm{BAB}}}{\frac{1}{2}\, n_{\mathrm{AAB+BAA}} + n_{\mathrm{BAB}}}$$

$$n_{\mathrm{B}} = \frac{n_{\mathrm{BBB}} + n_{\mathrm{ABB+BBA}} + n_{\mathrm{ABA}}}{\frac{1}{2}\, n_{\mathrm{ABB+BBA}} + n_{\mathrm{ABA}}}$$

The triad distribution is often studied by nuclear magnetic resonance spectroscopy (NMR).[3] Sometimes, the triad distribution can also be studied by infrared spectroscopy (IR).[5,6] Pyrolysis gas chromatography (Py−GC) is another technique that has been developed for trimer intensity studies in recent years.[7,8] Each technique has different advantages and weakness in terms of sample preparation, spectrum resolution, and level of interference.

Py−GC[9] is one of the important techniques used for polymer analysis. Py−GC is a technique that uses thermal energy (pyrolysis) to break down a polymeric chain to monomers, oligomers, and other fragments, followed by the separation of pyrolysates with gas chromatography (GC) and detecting with appropriate detectors. The flame ionization detector (FID) is one of the most commonly used detectors for quantitative analysis of pyrolysates. Mass spectrometry and mass selective detector (MSD) are the most commonly used detectors for identification. The intensities of monomers or monomer-related fragments are commonly used to obtain composition data.[10] The oligomers or oligomers-related fragments are used to deduce microstructure information.[11]

There are different approaches to model the copolymer chain microstructure such as Monte Carlo simulations based on the copolymerization kinetics.[12] This type of approach is based on the kinetics of the copolymerization theory to obtain certain parameters such as relative reactivity ratio to predict the probability of each

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monomer in the copolymer chain. A computer program can be written to virtually create a polymer chain as a result of this copolymerization kinetic model. A simulated polymeric chain can be further used to study the characteristics of polymer chain microstructure. All indirect methods used in the experimental polymer characterization such as counting the triad abundance as well as calculating the "number-average sequence length" can also be obtained by counting the monomers of the simulated copolymer chain.

In this study, a set of styrene and butyl acrylate copolymers with different composition and/or different microstructure has been synthesized and analyzed by Py−GC to obtain the trimer intensity scheme as well as the "number-average sequence length" values for each polymer. This experimental set of trimer intensity values as well as the "number-average sequence length" values, have been matched with a simulated set of triad intensity profiles and the "number-average sequence length" values that are obtained from a set of Monte Carlo simulated copolymer chains. If the experimental and simulated triad intensity profiles and the "number-average sequence length" values match, then monomer arrangement information on the real polymer can be explored based on the polymeric chain created by the Monte Carlo simulation.

Experimental Section

Emulsion Polymers. Most of the homogeneous emulsion polymers were synthesized in our laboratories. The polymer was synthesized based on procedures given in an experimental polymer textbook.[13] The styrene and butyl acrylate monomers were used along with sodium lauryl sulfate (used as surfactant) and ammonium persulfate (used as an initiator or free radical generator) for emulsion polymerization. A portion of 10 wt % of monomers and water were mixed at the beginning of the reaction. After 30 min of reaction, the rest of the monomers were setup to continually feed for another 150 min. Until all of the monomer was used, the reaction ran for another 60 min. The overall reaction was kept under nitrogen atmosphere, agitated with a mechanical stirrer, and kept at 80 °C with a water bath. The final product was a white emulsion polymer. After unreacted monomer was stripped out, the overall conversion was calculated to be approximately 80%. The partially random or partially structured copolymer was synthesized in a similar way, except monomers were sequentially and alternately fed.

Py−GC Conditions. Samples of polymer were carefully deposited into a quartz tube. The quartz tube was put into an off-line pyrolysis interface for 5 min at 300 °C to evaporate any nonpolymeric material (water, unreacted reagents). After this cleaning procedure, the quartz tube was equilibrated for 5 min in a 300 °C interface connected to the injection port of a Hewlett-Packard (HP) model 6890 gas chromatograph equipped with a FID. The samples were pyrolyzed (CDS 2000 Pyroprobe, Pt coil) at a calibrated temperature of 700 °C. The coil was heated to the calibrated temperature at 20 °C/ms and held at the set temperature for a 20-s interval. The pyrolysis products were split in the 300 °C injection port, with a 250:1 split ratio and a fast flow program (15 psi/0.2 min, 75 psi/min, to 90 psi/8.8 min) and were separated on a fused-silica capillary column (J & W Scientific DB-5, 10 m × 0.10 mm I. D., 0.4 μm film) using a fast temperature ramping program (50 °C/0.2 min, 100 °C/min, to 100 °C/0 min; 80 °C/min, to 140 °C/0 min; 60 °C/min, to 200 °C/0 min; 50 °C/min, to 280 °C/0 min; 40 °C/min, to 320 °C/5.2 min) and then detected by a FID.

Monte Carlo Simulation. The computer used in this Monte Carlo simulation was an IBM-PC, model 6862-M8U, with Pentium II/300 MHz processor. The program language used was FORTRAN. The FORTRAN compiler used was Pro Fortran Version 6.0 from Absoft Corp (Rochester Hills, MI). The program code and its explanation are available as Supporting Information. The simulation started with a hypothetical polymer chain with two units initially (butyl acrylate and then styrene). A random number function, uniformly distributed between 0 and 1, was used to determine the next unit in the chain. The relative reactivity ratio, combined with the unreacted monomer ratio defines the level of switching. If the random number was smaller than the level of switching, then the styrene monomer unit was attached to the growing polymer chain; otherwise, the butyl acrylate monomer unit was attached. The random number generation and the monomer attachment steps were repeated until 1000 monomer units were reached. The polymer chain with different numbers of monomer units has been tested for monomer composition and distribution; the chain with 1000 monomer units is long enough to reach the precision of the composition.[14]

Then, the triad intensity profile was generated. The number-average sequence length was calculated from the computer-simulated copolymers. The monomer abundance in each consecutive block was counted and tabulated in a data file. The values in the data file were transferred to an EXCEL spreadsheet to generate all bar graphs of the relative triad intensity plot as well as the monomer abundance in the consecutive block plot as shown in the figures.

Results and Discussion

Figure 1 shows a typical pyrogram of styrene and butyl acrylate copolymer (50/50 wt % composition). All timer peaks have been amplified and put in the inset. The "number-average sequence length" based on this set of trimers has been calculated. To express the trimer terms effectively, the letter S has been used to express styrene and letter B has been used to represent butyl acrylate. All trimers from the styrene and butyl acrylate copolymer can be expressed as SSS, SSB (or BSS), SBS, BSB, BBS (or SBB), and BBB.

To correlate the experimental results of trimer intensities to the triad distribution in a copolymer chain, the factors that affect the connection between these two quantities have to be understood. What are the relationship between triad intensity and the pyrolysis trimer-peak areas? Because the pyrolysis process applies thermal energy to break down the polymer chain into different fragments, the peak area obtained in the gas chromatography detector is a combination of the pyrolysis efficiency and the detector efficiency after the GC separation. Thus, two major factors dominate the relationship between triad distribution and trimer production. The first is the pyrolysis efficiency, which represents the probability/efficiency of breakdown of a specific triad configuration to produce the corresponding trimer. The second is the detection efficiency, which results in various FID responses for the trimers. These two factors cannot be separated for most copolymer composition and structure determinations.

A parameter K can be used as a coefficient to express the relationship between the pyrolysis peak area and the triad distribution. This K value reflects this combination of factors of pyrolysis efficiency and GC detector efficiency. It is important to know that the relative magnitude of K values within the styrene centered trimers as well as the butyl acrylate centered trimers because the K values will directly affect the result of the "number-average sequence" calculation. These K values can be obtained by calibrating through copolymers with known composition. The statistic (random) copolymer of known composition standards is preferred because it produces all trimer peaks allowing good calibration. The relationship between trimer production

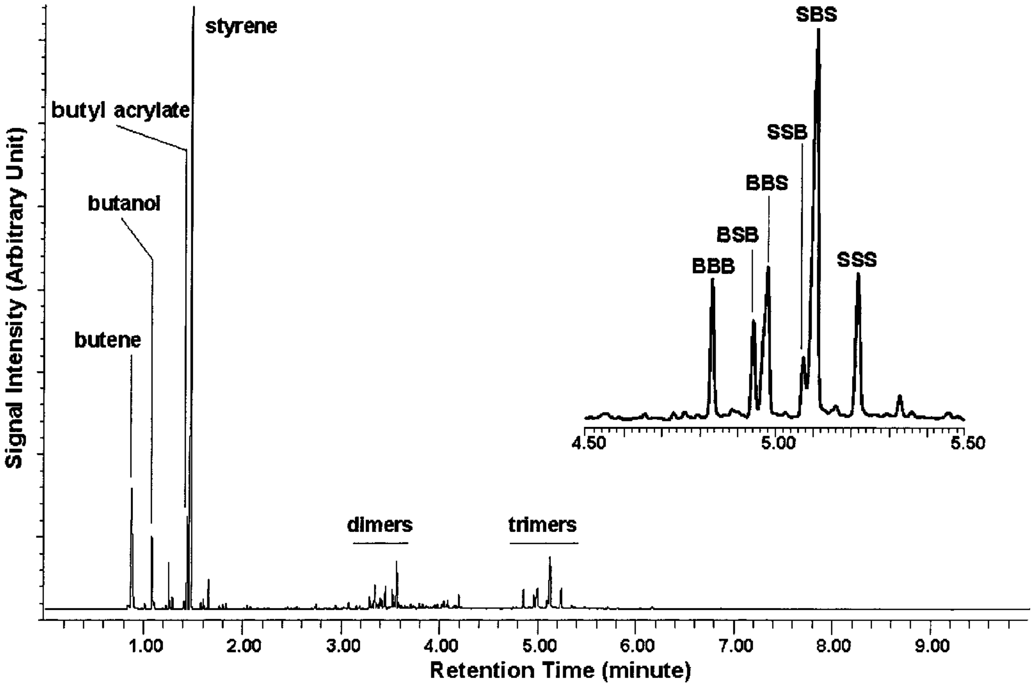

Figure 1. Pyrogram of styrene and butyl acrylate copolymer (50/50 wt % composition).

and triad distribution can be expressed as

experimental trimer peak intensity × K_n → triad distribution in the polymer

K_n is equal to the combination of pyrolysis efficiency and detection efficiency. The triad distribution in the polymer and the trimer peak intensities from pyrolysis can be written as

SSS peak intensity × K_{S1} → SSS distribution in the polymer

SSB peak intensity × K_{S2} → SSB distribution in the polymer

SBS peak intensity × K_{S3} → SBS distribution in the polymer

BSB peak intensity × K_{B3} → BSB distribution in the polymer

BBS peak intensity × K_{B2} → BBS distribution in the polymer

BBB peak intensity × K_{B1} → BBB distribution in the polymer

after calibration by pyrolyzing different known compositions of styrene and butyl acrylate copolymers. The set of K_n values for styrene and butyl acrylate copolymers can be obtained[4] and they are $K_{B1} = K_{B2} = K_{B3}$ and $3K_{S1} = K_{S2} = K_{S3}$. With this information, the relative trimer intensity can be plotted from Py–GC experimental results, and the "number-average sequence length" can also be calculated.

When a Monte Carlo simulation of a copolymerization reaction is perfomed, a suitable kinetic model must be established first. In this study, the penultimate model (second-order Markovian) has been chosen for the copolymerization kinetics model. The most common set of equations to express the copolymerization reactions for styrene and butyl acrylate copolymers can be expressed as

$$-M_BM_B^\bullet + M_B \xrightarrow{k_{BBB}} -M_BM_BM_B^\bullet$$

$$-M_BM_B^\bullet + M_S \xrightarrow{k_{BBS}} -M_BM_BM_S^\bullet$$

$$-M_SM_B^\bullet + M_B \xrightarrow{k_{SBB}} -M_SM_BM_B^\bullet$$

$$-M_SM_B^\bullet + M_S \xrightarrow{k_{SBS}} -M_SM_BM_S^\bullet$$

$$-M_BM_S^\bullet + M_B \xrightarrow{k_{BSB}} -M_BM_SM_B^\bullet$$

$$-M_BM_S^\bullet + M_S \xrightarrow{k_{BSS}} -M_BM_SM_S^\bullet$$

$$-M_SM_S^\bullet + M_B \xrightarrow{k_{SSB}} -M_SM_SM_B^\bullet$$

$$-M_SM_S^\bullet + M_S \xrightarrow{k_{SSS}} -M_SM_SM_S^\bullet$$

where M_S expresses the styrene monomer unit and M_B expresses the butyl acrylate monomer unit. k_{BBB}, k_{SBB}, k_{BSS}, and k_{SSS} are the rate constants for the self-propagating reactions, and k_{BBS}, k_{SBS}, k_{BSB}, and k_{SSB} are the corresponding cross-propagating rate constants. The terms of relative reactivity ratios can be defined as $r_{BB} = k_{BBB}/k_{BBS}$, $r_{SB} = k_{SBB}/k_{SBS}$, $r_{BS} = k_{BSS}/k_{BSB}$, and $r_{SS} = k_{SSS}/k_{SSB}$. Under the assumptions of steady-state conditions, the propagating reactivity is independent of chain length and depends only on the nature of the two terminal units. Thus, a computer program can be written to simulate the chain growth.

When a set of r_{BB}, r_{SB}, r_{BS}, r_{SS} and the concentrations of both monomers have been selected, the program will simulate a polymerization reaction to create a copolymer chain. The abundance of each monomer in consecutive monomer block and the total number of each different triad can be obtained by analyzing this copolymer chain. The relative triad intensity of all triads can be plotted

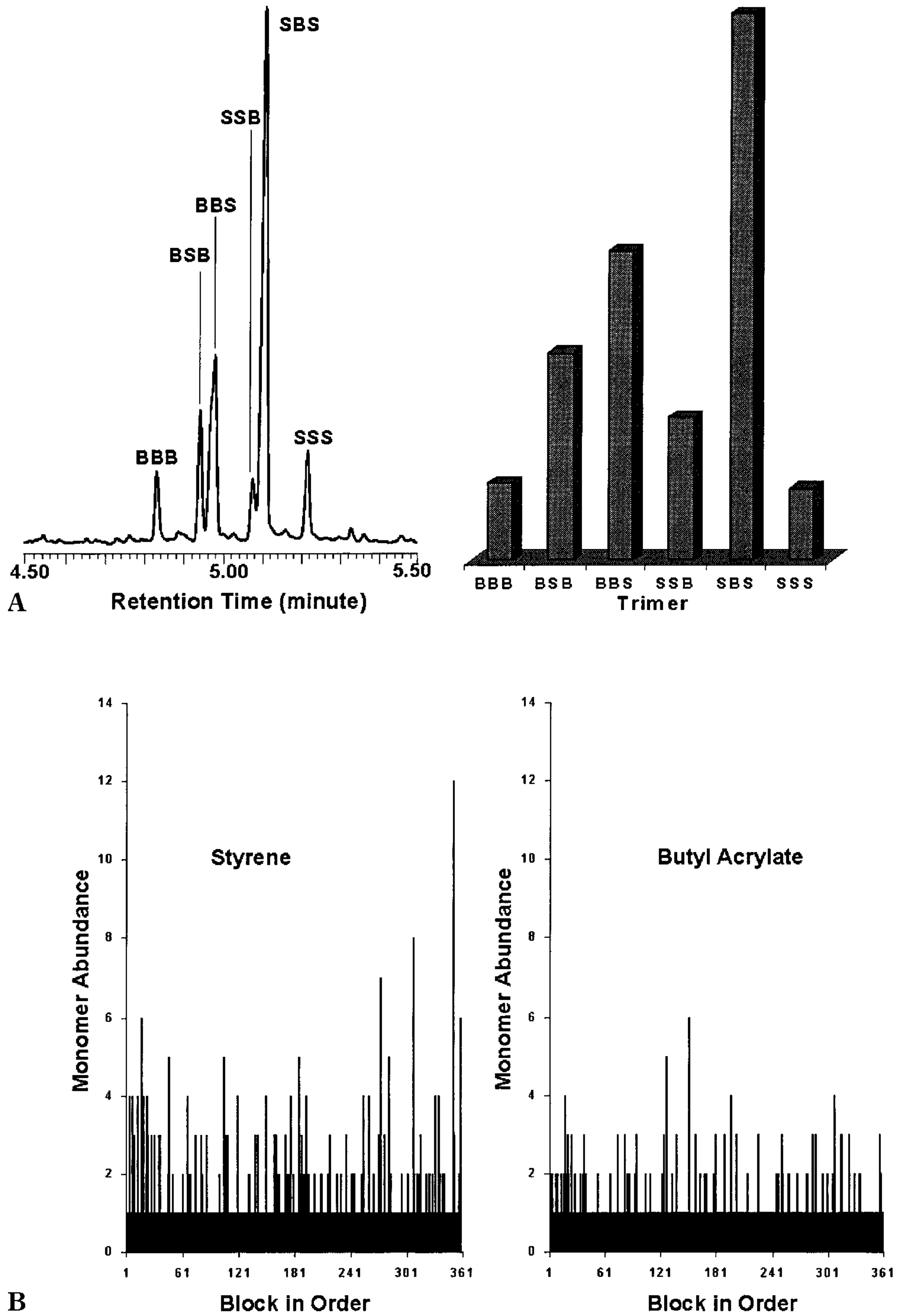

Figure 2. (A) Relative triad intensity of an experimental result and the simulated result for a styrene and butyl acrylate copolymer with 50/50 wt % composition. (B) Monomer abundance of styrene and butyl acrylate in the consecutive block order.

and the "number-average sequence length" can be calculated.

What condition is required for a computer-simulated copolymer chain to be deemed identical to a real copolymer chain? Two important pieces of information can serve as an indicator. One is the triad intensity profile, and the other is the "number-average sequence length" value. Both of these values can be measured or calculated from the experimental and Monte Carlo simulated copolymer chain. In the Monte Carlo simulation, the copolymer chain microstructure was determined by the set values of relative reactivity ratios, r_{BB}, r_{SB}, r_{BS}, and r_{SS}, and the monomer concentration. The choice of a correct set of values of the relative reactivity ratios to represent the experimental copolymerization reaction is difficult. However, it may be achieved by a trial-and-error method. If a set of relative reactivity ratio values is used and the information generated from the simulated copolymer matches the Py−GC experimental results, then the set values may be very close to real relative reactivity ratios. More confidence in the relative reactivity ratios is provided when the results from simulated copolymers with different composition created with the same set of relative reactivity ratio values all matches the experimental results. The exploration of monomer arrangement in a copolymer chain can be accomplished in a simulated copolymer chain that is compatible with the real copolymer chain.

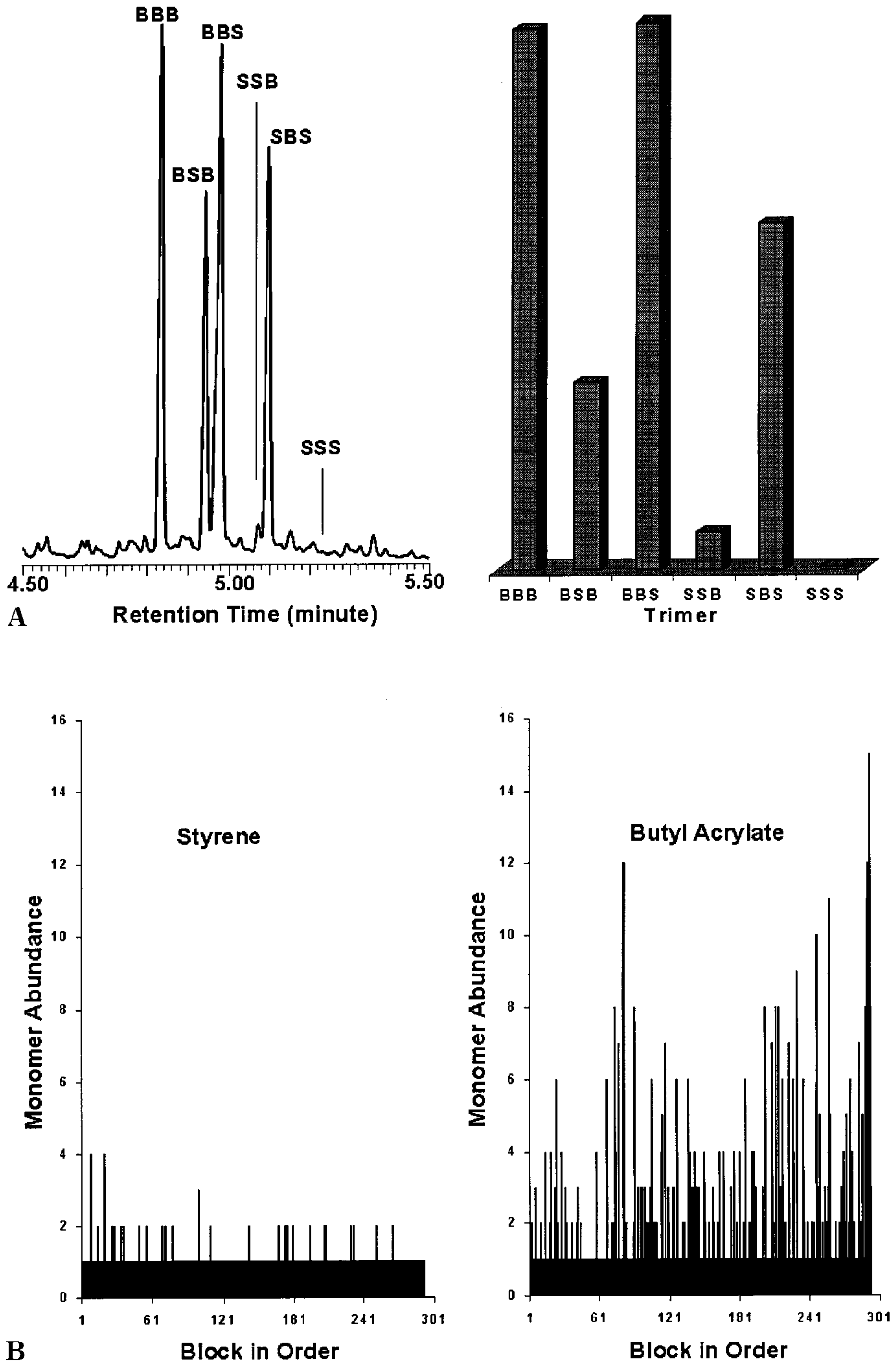

Figure 3. (A) Relative triad intensity of an experimental result and the simulated result for a styrene and butyl acrylate copolymer with 28/72 wt % composition. (B) Monomer abundance of styrene and butyl acrylate in the consecutive block order.

In this styrene and butyl acrylate copolymer case, there have been tabulated data with references of monomer reactivity ratio of r_1 and r_2 for the styrene and butyl acrylate copolymer system associated with the terminal (or first-order Markov) copolymerization model.[15] In this study, a set of $r_{BB} = 0.6$, $r_{SB} = 0.3$, $r_{BS} = 0.3$, and $r_{SS} = 0.6$ have been chosen for Monte Carlo simulation. The "number-average sequence length" calculation from simulation matched very well with the Py–GC experimental values. However, in the Py–GC experimental results, the styrene-centered trimers (SSS, SSB, and SBS) may have a different pyrolysis and detection efficiency from the butyl acrylate centered trimers (BBB, BBS, and SBS). A coefficient has been applied (multiplied by a factor of 3) to the butyl acrylate centered triads (BBB, BBS, and SBS) in the simulated values to compensate the intensity difference. This multiplication will not change the "number-average sequence length" value of butyl acrylate because the coefficient will be canceled in numerator and denominator during the "number-average sequence length" calculation.

Figure 2A shows a relative trimer intensity plot of the experimental results and the simulated results of the triad intensity for a styrene and butyl acrylate 50/50 wt % composition statistical copolymer. The "number-average sequence length" from the Py–GC experimental

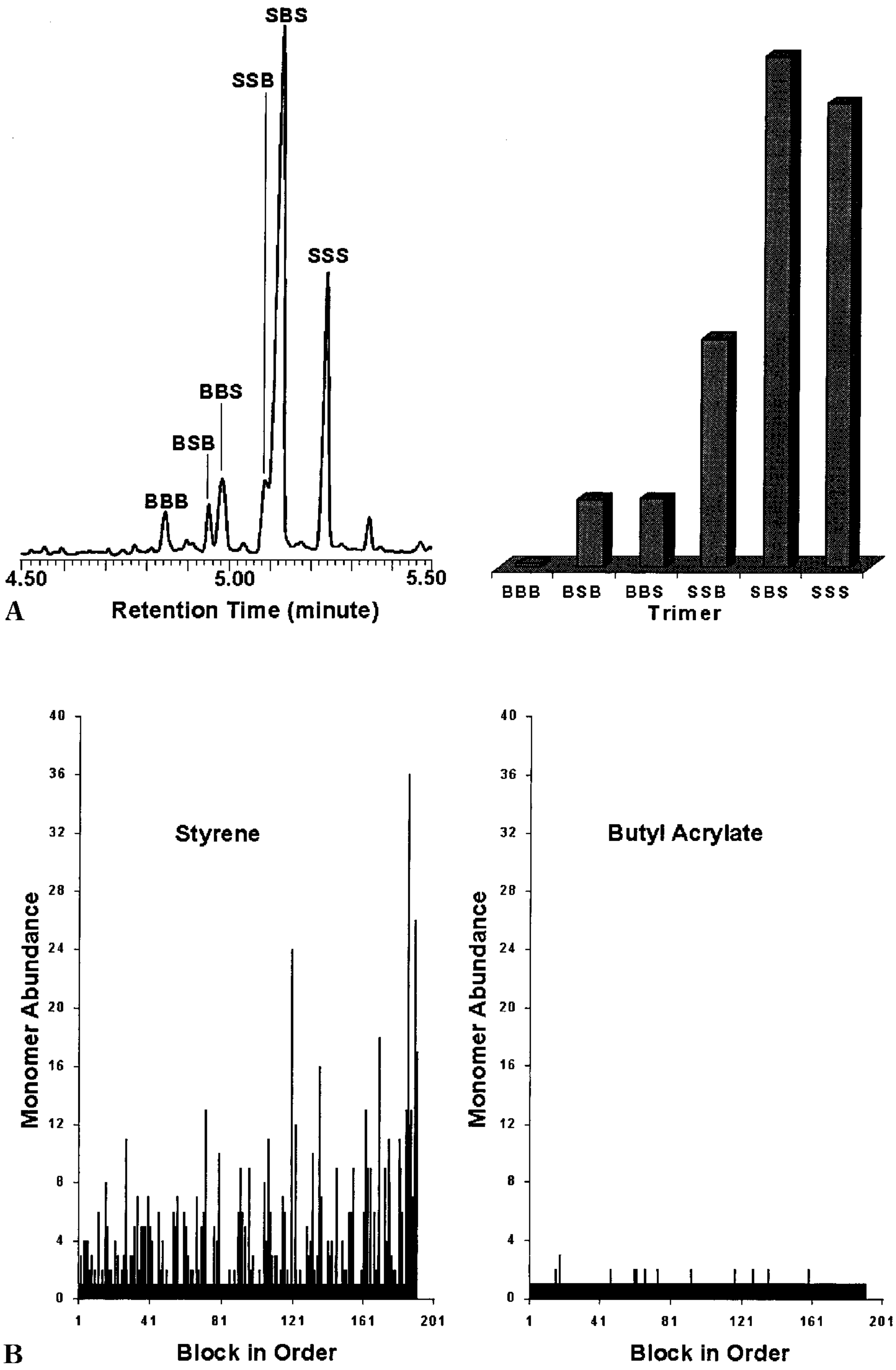

Figure 4. (A) Relative triad intensity of an experimental result and the simulated result for a styrene and butyl acrylate copolymer with 76/24 wt % composition. (B) Monomer abundance of styrene and butyl acrylate in the consecutive block order.

results are $N(S) = 1.49$ and $N(B) = 1.28$[11] and the simulated results are $N(S) = 1.49$ and $N(B) = 1.28$. Figure 2B shows the monomer abundance of styrene and butyl acrylate in the consecutive block order. The monomer abundance defines as the number of monomers in that block. The block in order means in the x-axis, the plot is shown for first, second, third, and fourth ... blocks of a specific monomer in the polymeric chain. Both monomers have formed approximate 360 blocks sequentially alternating with each other. For butyl acrylate, there are 293 blocks that are single monomer units, 41 blocks are two monomer units, and 25 blocks are more than two monomer units. For styrene, there are 266 blocks that are single monomer units, 46 blocks are two monomer units, and 46 blocks are more than two monomer units. On the basis of the fact that more than 80% of butyl acrylate monomer units in the copolymer as single unit block and so as 74% of styrene monomer unit, both monomers are well dispersed in the copolymer chain. However, how are the blocks that contain two and more than two monomer units distributed in the copolymer? This question can be answered by the monomer abundance in the consecutive block plot, and this cannot be accomplished by experimental measurement. The monomer abundance in the consecutive block plot fully demonstrates the monomer arrangement in the polymer chain.

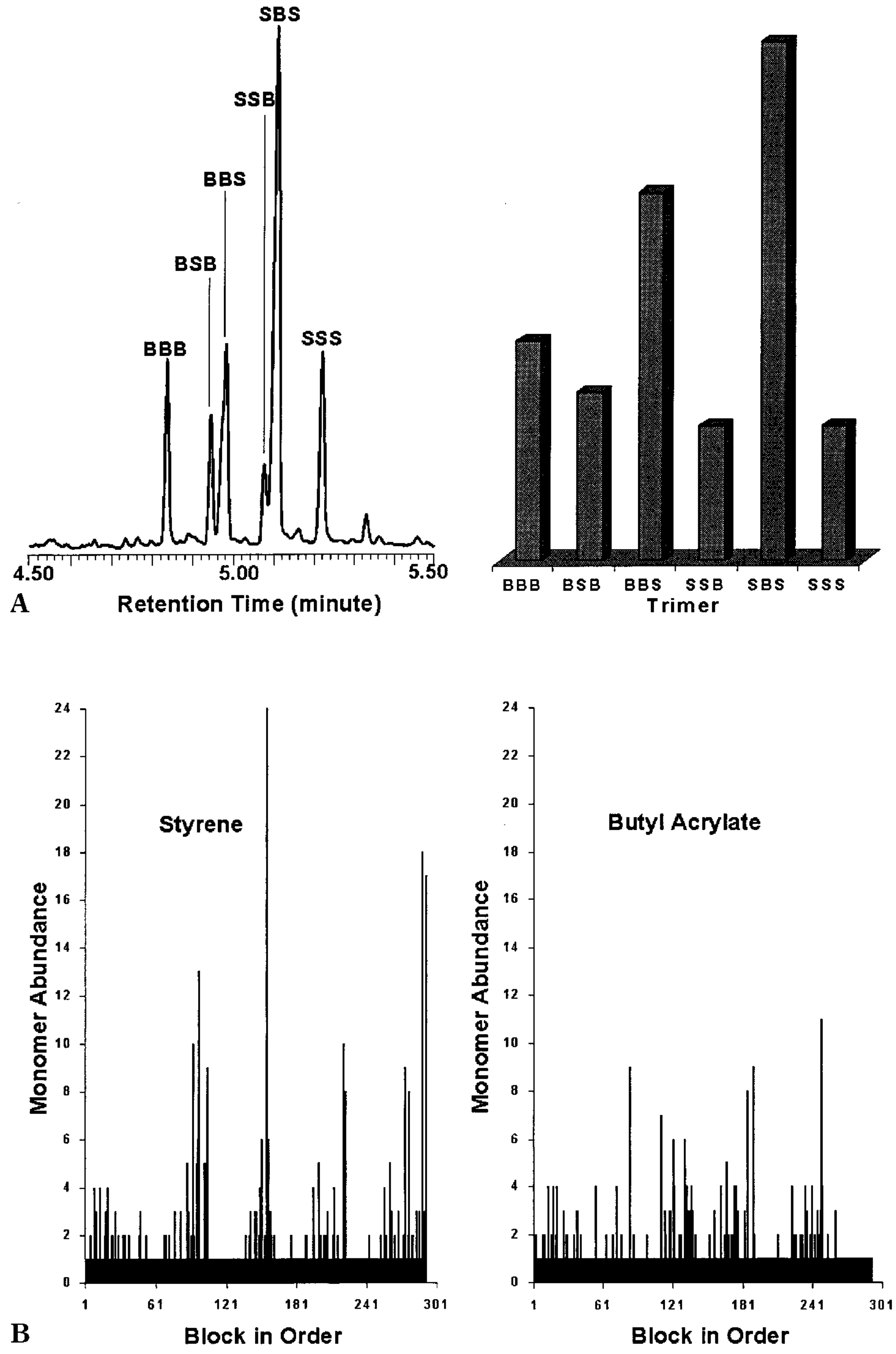

Figure 5. (A) Relative triad intensity of an experimental result and the simulated result for a styrene and butyl acrylate copolymer with 50/50 wt % composition. (B) Monomer abundance of styrene and butyl acrylate in the consecutive block order.

What kind of distribution can be expected if the number of different monomers has a large difference? Figure 3A shows relative trimer intensity plot of experimental results and the simulated result of triad intensity for a styrene and butyl acrylate statistical copolymer with 28/72 wt % composition. The "number-average sequence length" from the experimental results are $N(S) = 1.11$ and $N(B) = 2.35$[11] and the simulated results are $N(S) = 1.11$, $N(B) = 2.31$. Figure 3B shows the monomer abundance of styrene and butyl acrylate in the consecutive block order. Both monomers have formed approximately 285 blocks sequentially alternating with each other. For butyl acrylate, there are 164 blocks that are single monomer units, 49 blocks are two monomer units, and 80 blocks are more than two monomer units. For styrene, there are 265 blocks that are single monomer units, 24 blocks contain two monomer units, and three blocks contain more than two monomer units. On the basis of the composition, the number ratio of the styrene monomer to the butyl acrylate monomer is about 1:2. Thus, 94% of the styrene exists in the copolymer chain as a single unit block, which demonstrates the statistical nature (randomness) of this copolymer chain microstructure. Only three blocks contain three or more styrene monomer units, the same fact is also shown in the trimer intensity plot in Figure 3A. In Figure 3B, the uniform distribution of butyl acrylate blocks that contain two or more monomer units throughout the entire copolymer chain confirms that statistical conditions exist in this copolymerization.

In the other extreme, Figure 4A shows a relative trimer intensity plot of experimental and the simulated results of triad intensity for a styrene and butyl acrylate statistical copolymer with 76/24 wt % composition. The “number-average sequence length” from the experimental results are $N(S) = 4.21$, $N(B) = 1.07^{11}$ and the simulated results are $N(S) = 4.17$, $N(B) = 1.07$. Figure 4B shows the monomer abundance of styrene and butyl acrylate in the consecutive block order. Both monomers have formed 194 blocks sequentially alternating with each other. For butyl acrylate, there are 182 blocks that are a single monomer unit, 11 blocks are two monomer units, and one block is more than two monomer units. For styrene, there are 72 blocks that exist as single monomer units, 31 blocks are two monomer units, and 91 blocks are more than two monomer units. Instead of a copolymer possessing a large amount of butyl acrylate, as in the last example, this one has more styrene monomer. The very low intensity of butyl acrylate can be seen in both parts A and B of Figure , reflecting the probability of trimer formation being low because of the low amount of monomer. The number ratio of styrene monomer to the butyl acrylate monomer is about 4:1, which causes the styrene blocks to sometimes accumulate to more than 20 units (as in Figure 4B).

The advantages of comparing both the experimental data and Monte Carlo simulation results not only in the complete copolymer chain definition but also in the copolymer chain microstructure design and prediction. For example, if a copolymer with 50/50 wt % composition was desired, and one wants the copolymer microstructure to have a dispersed distribution but not as random as the statistical copolymer, one way to approach this design is by sequentially and alternately feeding the monomers during the copolymerization reaction. Certain parameters can be adjusted to control the “degree of randomness” or the “degree of structure”, which include the timing of alternate feeding and the steps/amount of feeding.

Figure 5A shows relative trimer intensity plot of experimental data and the simulated result of triad intensity for a styrene and butyl acrylate copolymer 50/50 wt % composition. The Monte Carlo simulation in this case was accomplished by adding about 20% of each monomer in the beginning, then, sequentially and alternately adding 20% of each monomer during the copolymerization reaction between 25% to 85% conversions. The detailed program code is available in the Supporting Information. The “number-average sequence lengths” from the experimental results are $N(S) = 1.88$, $N(B) = 1.59$, and the simulated results are $N(S) = 1.86$, $N(B) = 1.58$. Figure 5B shows the monomer abundance of styrene and butyl acrylate in the consecutive block order. Both monomers have formed 291 blocks that sequentially alternate with each other. For butyl acrylate, there are 215 blocks that are single monomer units, 37 blocks are two monomer units, and 39 blocks are more than two monomer units. For styrene, there are 207 blocks that are single monomer units, 41 blocks are two monomer units, and 43 blocks are more than two monomer units. Comparing Figure 2A with Figure 5A, the most significant difference is the triad and trimer intensities of pure styrene and butyl acrylate. The increased intensities in both pure triads/trimers indicate that there are more blocks with multiple monomers in the sequential feed sample. However, the relative intensity of those hybrid trimers is kept approximately the same, indicating that the copolymer chain microstructure still contains a certain degree of randomness. The total number of blocks for each monomer changed from 358 blocks (totally random) to 291 blocks (partially random). However, the percentage of single unit blocks slightly decrease (from 80% to 74% for butyl acrylate and from 74% to 71% for styrene); at the same time, the percentage of blocks with more than two units increased (from 7% to 13% for butyl acrylate and from 13% to 15% for styrene). All these facts indicated a decrease of randomness in the copolymer microstructure. Examination of Figure 5B shows that there are long blocks formed periodically during the copolymer chain growth. These long blocks were formed during the alternating feeding process are clearly illustrated by the sequentially and alternately feeding effect in the copolymer chain microstructure. The existence of these long blocks also gives the explanation for the increased intensities of the pure trimer intensities.

Conclusions

A method has been developed to utilize the experimental data from the Py−GC, integrated with the results from the Monte Carlo simulation to characterize a copolymer chain microstructure. The bridge between Py−GC and the Monte Carlo simulation is the relative trimer peak intensities as well as the “number-average sequence length” values. By appropriate selection of the set of values of relative reactivity ratio and monomer concentration, the triad intensity profile from a Monte Carlo simulation can be matched with the Py−GC experimental result of relative trimer intensity scheme. If the triad intensity profile and the values of “number-average sequence length” are a unique parameter set for every different chain structure, all the monomer arrangement information on the real polymer chain can be explored based on the chains created by the Monte Carlo simulation. This method can also be used as a design tool for the desired copolymer chain microstructure. The synthesis of the partially random or partially structured styrene and butyl acrylate copolymer is a very good example. The development of this method makes it possible to extend microstructure determination beyond the instrumentation limit.

Supporting Information Available: The program code used in this study and text giving its explanation. This material is available free of charge via the Internet at http://pubs.acs.org.

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