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Compositional Heterogeneity in Polymers: Computer Simulation Approaches[†]

H. N. Cheng,* Stanley B. Tam,[‡] and Leo J. Kasehagen

Research Center, Hercules Incorporated, Wilmington, Delaware 19894

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ABSTRACT: A family of computer programs (called PODIS) has been written that permits compositional heterogeneity in copolymers to be directly computed. Different sources of compositional heterogeneity have been specifically addressed by separate programs. Included in the treatments are statistical heterogeneity, conversion heterogeneity, multistate heterogeneity, and compositional heterogeneity due to fluctuations in polymerization process parameters. Through these means, predicted chemical composition distributions have been made for linear low-density polyethylene, styrene/ethyl methacrylate copolymers, and styrene/methyl acrylate copolymers. Computer simulation permits many observed compositional features of these copolymers to be understood.

Introduction

Compositional heterogeneity in copolymers has attracted increasing attention. A number of papers have been published recently[1–9] on this subject. It was pointed out[1] that at least four types of compositional heterogeneity can be distinguished: (1) statistical or instantaneous heterogeneity,[10,11] where compositional variation arises from random combinations of comonomer placements on polymer chains; (2) conversion heterogeneity,[12–15] where differences in the reactivity ratios of the comonomers cause copolymers with different compositions to be made at different conversion levels; (3) multistate heterogeneity,[16–18] where different copolymer chains are made at different initiator/catalytic sites, each with its own set of comonomer reactivity ratios; and (4) process heterogeneity,[1,2] where fluctuations in polymerization process parameters (e.g., temperature, monomer feed rates, agitation speed, solution viscosity, and particle size) cause minor changes in copolymer composition.

Earlier publications involving computer approaches have included only statistical and conversion heterogeneities. For example, Chan and Meyer,[19] O'Driscoll and Knorr,[20] and Prochazka and Kratochvil[21] have written computer programs to demonstrate the effect of conversion on compositional broadening. Mirabella[22] showed the molecular weight dependence of copolymer composition by a computer approach. Other computer approaches have been published by Harwood et al.,[23,24] O'Driscoll et al.,[25] and Motoc et al.[26,27] Theoretical studies have been made with the help of computers.[6–9]

In this work we have examined the general problem of compositional heterogeneity through a systematic computer approach. Through computer synthesis we are able to study all four types of compositional heterogeneity. A family of computer programs (PODIS) has been written and was designed to visualize the POlymer DIStribution in the presence of various types of heterogeneities. The programs are flexible and allow the simulation and the prediction of a large number of copolymer systems. Through appropriate use of this synthetic approach, a better understanding can be obtained of the nature of the compositional heterogeneities in many copolymers.

Results and Discussion

I. Statistical Heterogeneity. Exact Solution. Compositional heterogeneity due to statistical variation in comonomer placements can be simulated exactly through the use of reaction probability models. The statistical models commonly employed for this purpose are Bernoullian and first- and second-order Markovian models.[28,29] The second-order Markovian model will be treated here; the lower order models can be chosen with the appropriate assignments of reaction probability values. We follow the conventional nomenclature,[29] $\alpha = P_{aaa}$, $\bar{\alpha} = P_{aab}$, $\beta = P_{aba}$, $\bar{\beta} = P_{abb}$, $\gamma = P_{baa}$, $\bar{\gamma} = P_{bab}$, $\delta = P_{bba}$, and $\bar{\delta} = P_{bbb}$ where P_{aab} is the reaction probability of comonomer B adding to a propagating chain terminating in –AA in an AB copolymer. For dimers the reaction probabilities and the compositions are as follows:

dimer	content of A, %	probability
AA	100	$\gamma\delta$
AB	50	$2\bar{\alpha}\delta$
BB	0	$\bar{\alpha}\bar{\beta}$

Thus, the compositional heterogeneity for dimerization is very large. The content of A spreads from 0% (the BB dimer) to 100% (the AA dimer). The average A content is $(\gamma\delta + \bar{\alpha}\delta)/(\gamma\delta + 2\bar{\alpha}\delta + \bar{\alpha}\bar{\beta})$. The compositional spread is due to statistical heterogeneity only.

For trimers, the reaction probabilities and compositions are as follows:

trimer	content of A, %	probability
AAA	100	$\alpha\gamma\delta$
AAB	67	$2\bar{\alpha}\gamma\delta$
BAB	33	$\bar{\alpha}\bar{\gamma}\delta$
ABA	67	$\bar{\alpha}\bar{\beta}\delta$
BBA	33	$2\bar{\alpha}\beta\delta$
BBB	0	$\bar{\alpha}\bar{\beta}\bar{\delta}$

The statistical compositional heterogeneity is still sizable. Similar expressions can be written for tetramers where 10 different permutations of A and B are possible. For an n-mer, we would need to consider $(2^{n-1} + 2^m)$ permutations, where $m = n/2$ if n is even and $m = (n - 1)/2$ if n is odd. The computational effort would increase substantially.

[†] Hercules Research Center Contribution No. 2121.

[‡] Present address: Lord Corp., 2000 West Grandview Blvd., Erie, PA 16514.

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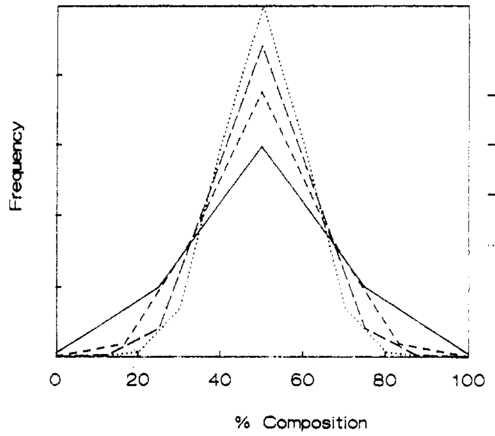

Figure 1. Theoretical composition distributions of n-mers, where n = 4, 6, 8, and 10. Simulation was done through the program PODIS1: first-order Markovian model, P_{ab} = 0.731, P_{ba} = 0.731.

To facilitate this computation, we wrote a computer program, PODIS1. The following dimer sequences serve to start the polymer chain:

starting units	probability
AA	$F_1 = \gamma\delta$
AB	$F_2 = \bar{\alpha}\delta$
BA	$F_3 = \bar{\alpha}\delta$
BB	$F_4 = \bar{\alpha}\bar{\beta}$

The probability for any sequence can be calculated by taking consecutive second-order Markovian probabilities, first from right to left and then from left to right. An example illustrates this calculation:

$$\begin{aligned}(\mathrm{ABAAB}) &= F_2P_{\mathrm{aba}}P_{\mathrm{baa}}P_{\mathrm{aab}} + F_3P_{\mathrm{baa}}P_{\mathrm{aab}}P_{\mathrm{aba}} \\ &= F_2\beta\gamma\bar{\alpha} + F_3\gamma\bar{\alpha}\beta \\ &= \bar{\alpha}^2\beta\gamma\delta + \bar{\alpha}^2\beta\gamma\delta\end{aligned}$$

The first term represents the probability of a chain growing from left to right (A → B → A → A → B); the second term is for a chain growing from right to left (B → A → A → B → A). The reversibility character[30] of the second-order Markovian model ensures that the two values are the same.

Whereas the solution is exact in this approach, computation becomes increasingly time-consuming as n increases, even for a computer. On a personal computer (Model 486), it takes 45 min to calculate the compositional distribution of polymers with a degree of polymerization (n) of 10. Polymer chains longer than 10 monomer units would take too much time to calculate by this means.

As an example of this approach, the compositional distributions of a tetramer to a decamer (n = 4–10) are given in Figure 1. In all cases, a first-order Markovian model is assumed: P_{ab} = 0.731 and P_{ba} = 0.731. As expected,[10] the compositional spread decreases with increasing degrees of polymerization.

Monte Carlo Simulation. An alternative approach that can be applied to polymer chains of much higher n values is the Monte Carlo simulation.[28] A computer program, called PODIS2, has been written to carry out the computations.

In this approach, the computer literally builds up a fixed number of polymer chains with prescribed molecular weights. Arbitrary maxima of 1000 polymer chains and 35 000 monomer units per chain have been chosen for the convenience of the personal computer used. These maxima can be readily changed if needed. A logic diagram showing the relationships between different parts of the program is given in Figure 2.

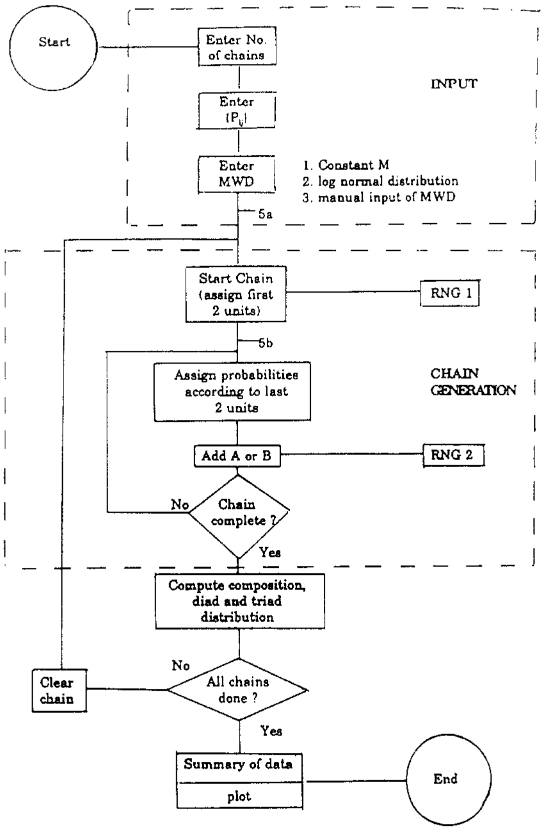

Figure 2. Logic diagram for program PODIS2.

The program PODIS2 starts with a fixed number of polymer chains corresponding to the initiator concentrations. The same starting units (dimer sequences) are used as in PODIS1 to start the probability product series. Three options are available for the degree of polymerization. We can use a constant value for the entire sample (i.e., monodisperse in the molecular weight distribution). We can feed in the parameters corresponding to a log normal distribution of molecular weights.

$$f(\ln M) = \frac{1}{(2\pi)^{1/2}\sigma}\exp\left[-\frac{\{\ln (M/M_0)\}^2}{2\sigma^2}\right]$$

The parameters can be either M_0 and σ, or M_n and M_w derived from the log normal distribution.[31] The third option is to input manually pairs of values corresponding to an observed molecular weight distribution (e.g., the output of size-exclusion chromatography, SEC).

A random number generator (RNG) is used to choose a starting unit. A second random number generator is used to add additional comonomer units. In the second RNG, comparison is made with the Markovian probabilities for propagation (α, β, γ, and δ in the second-order Markovian model and P_{ab} and P_{ba} in the first-order Markovian model). When the polymer chain has grown to the prescribed number of comonomer units (dictated by the molecular weight requirements), the chain growth stops. The chain is now counted for composition [(A) and (B)], diad sequences [(AA), (AB), and (BB)], and triad sequences [(AAA), (AAB), etc.]. All the units of this chain are then erased, and a new chain is initiated. This process continues until all the chains have been generated and their compositions and sequences accounted for.

As written, the program PODIS2 is applicable to a continuous polymerization process at steady state. There would be no complication from conversion. We assume

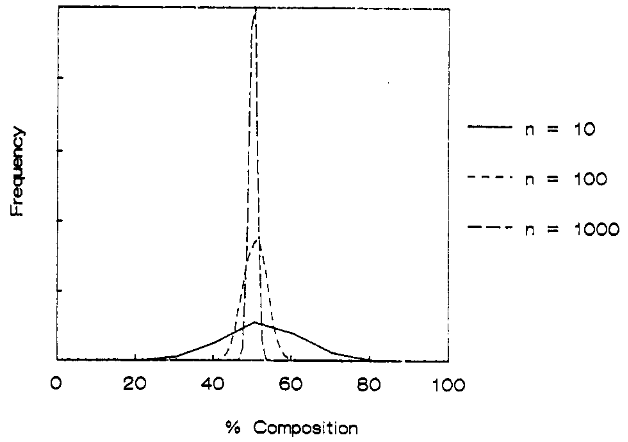

Figure 3. Theoretical composition distributions of n-mers, where $n = 10, 100$, and 1000. Simulation was done through the program PODIS2: first-order Markovian model, $P_{ab} = 0.731$, $P_{ba} = 0.731$.

that one set of Markovian probabilities can adequately simulate the entire polymerization. Furthermore, fluctuations in temperature, comonomer feed, and other process variables are small. Thus, the only source of compositional heterogeneity is *statistical*.

As an example of program PODIS2, the compositional distributions of a first-order Markovian copolymer with $P_{ab} = 0.731$ and $P_{ba} = 0.731$ with $n = 10, 100$, and 1000 are given in Figure 3. Stockmayer[10] has earlier shown that the distribution function is Gaussian with standard deviation σ_F, where

$$\sigma_F^2 = \bar{F}(1-\bar{F})[1 + 4\bar{F}(1-\bar{F})(r_A r_B - 1)]^{1/2}/n$$

where $\bar{F}$ is the average copolymer composition. This inverse relationship between σ_F^2 and n is indeed observed in this simulation.

II. Conversion Heterogeneity. The next stage of software development is to keep the features of PODIS2 and to introduce conversion heterogeneity on top of statistical heterogeneity. This would correspond to a copolymerization carried out in a batch mode. The computer program that permits this type of simulation is called PODIS3.

The program PODIS3 is similar to the program PODIS2 except that the reaction probabilities are changing as polymerization proceeds. Thus, both the initiator probabilities and the propagation probabilities vary with conversion.

$$\alpha = \frac{r_A x}{1 + r_A x}, \quad \beta = \frac{1}{1 + r_B'/x}$$

$$\gamma = \frac{r_A' x}{1 + r_A' x}, \quad \delta = \frac{1}{1 + r_B/x}$$

where $r_A = k_{AAA}/k_{AAB}$, $r_A' = k_{BAA}/k_{BAB}$, $r_B = k_{BBB}/k_{BBA}$, and $r_B' = k_{ABB}/k_{ABA}$, and $x = (A)/(B)$. Thus, whereas the reactivity ratios (r_i) are constant, x changes. When polymerization (simulation) starts, the computer program uses the initial feed concentration of A and B. As A and B are depleted in different rates, new values of (A) and (B) are calculated. From these updated values of (A) and (B), new values of α, β, γ, and δ are calculated and used in the chain generation process.

As an example of how PODIS3 works, we shall simulate the compositional heterogeneity observed in styrene/ethyl methacrylate (S/EMA) copolymers. Mori[4] has developed a liquid adsorption chromatographic method to determine the chemical composition distribution (CCD). A number of styrene/acrylate and styrene/methacrylate copolymers have been prepared in benzene at low conversions and analyzed. In a separate work, Tacx et al.[6] made copolymers of styrene/ethyl methacrylate in toluene and analyzed the CCD by a quantitative thin-layer chromatography/flame ionization detection method, using a concentration gradient elution technique for development. They prepared their polymers in high conversions. The key parameters for the two S/EMA copolymers are summarized below:

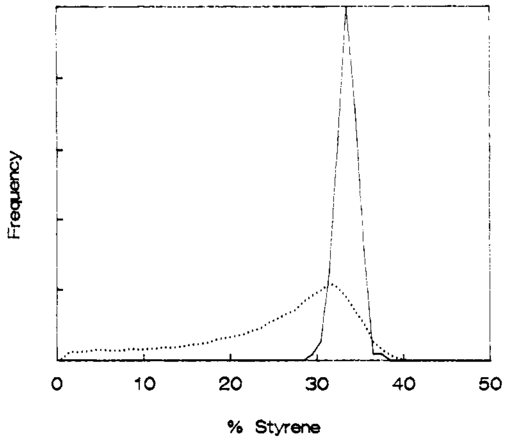

Figure 4. Predicted compositonal distributions of styrene/ethyl methacrylate copolymers. Solid line, 17.6% conversion; dotted line, 98.0% conversion (curve smoothed). Simulation was done through the program PODIS3; parameters are given in the text.

author	feed composn, mol %	reactivity ratio	M_n	M_w	convn, %
Mori[4] (SEMA III)	(S) = 24.6 (EMA) = 75.4	?	8.0×10^4	13.5×10^4	17
Tacx[6]	(S) = 24.8 (EMA) = 75.2	r_s = 0.49 r_{EMA} = 0.40	4.8×10^4	?	98

The two copolymers are sufficiently similar in feed composition and molecular weight and only differ significantly in conversion. Simulation is readily carried out using the same reactivity ratios for both polymers. In the case of Tacx copolymer, a constant M_n is assumed, whereas for the Mori polymer a log normal distribution of molecular weight is used. The CCD curves predicted from the program PODIS3 are given in Figure 4.

The importance of conversion to compositional heterogeneity is clearly demonstrated in Figure 4. At lower conversions, the copolymer composition is centered on 34 mol % styrene. At higher conversions, the composition drifts toward the lower styrene composition. It is of interest that the predicted CCD curves match very well with the CCD curves reported experimentally by Mori[4] and by Tacx et al.[6]

III. Multistate Heterogeneity. A further elaboration of this approach is to apply it to cases where different polymer chains are made at different propagating centers, each having its own reactivity ratios. The resulting polymer is really an in situ blend of several polymer components.

A simulation of such a polymer can be readily made by adding up the compositional distributions of individual components. The only requirement is that the reaction probabilities of the individual components be known. NMR spectra of the copolymers potentially contain this information. Recently, a systematic methodology has been developed that permits the NMR data of either whole polymers or polymer fractions to be analyzed and the

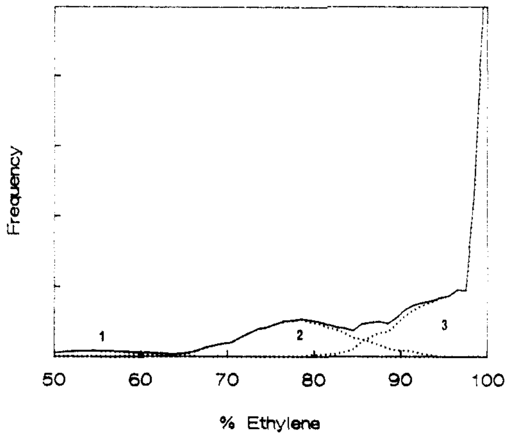

Figure 5. Predicted compositional distribution of an ethylene/1-butene copolymer (linear low-density polyethylene). Three components are assumed to be present. Solid line, overall composition; dotted lines, composition distribution of the three components. Simulation was done through program PODIS4; parameters are given in the text; a Gaussian broadening of σ = 0.06 was used.

reaction probabilities of multiple components to be unraveled.[32-36] These reaction probabilities can be used to carry out the simulations of compositional heterogeneity.

A separate computer program called PODIS4 has been written to carry out this simulation. Up to four components can be generated separately. Each component can be made by a continuous type of polymerization (PODIS2) or a batch-type (PODIS3). The molecular weight specifications are the same as in the separate PODIS2 and PODIS3 programs. The contributions from all the components are then added together.

As an example, the compositional distribution in an ethylene/1-butene copolymer will be predicted. Previously, Kuroda et al.[37] has made this copolymer, fractionated it, and analyzed the fractions by ^{13}C NMR. Cheng[34] studied their data and analyzed them via the computer-assisted analytical approach.[32,33] On the basis of that analysis, the copolymer can be considered to consist of three distinct components, two components obeying Bernoullian statistics and one component obeying first-order Markovian statistics.

component	model	probabilities	contribn, %
1	1st-order Markovian	P_{be} = 0.712 P_{eb} = 0.597	4.4
2	Bernoullian	P_b = 0.22	33.9
3	Bernoullian	P_b = 0.03	61.7

The copolymerization of ethylene and 1-butene can be readily simulated in the steady-state mode, and the predicted compositional distribution of this three-component polymer is given in Figure 5. The molecular weight values used were taken from Kuroda et al.[37] It is clear that the polymer covers a very broad compositional range. Component 3 is found at high ethylene contents, component 2 at 70–85% ethylene, and component 1 at about 50% ethylene. Note that an (arbitrary) Gaussian broadening of σ = 0.06 has been used.

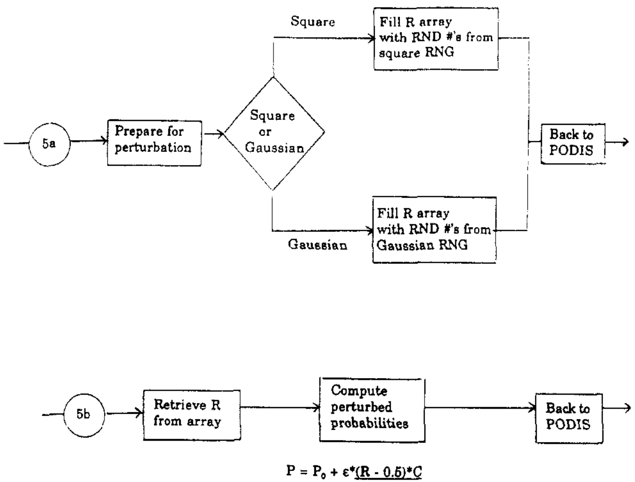

Figure 6. Logic diagram for the modifications needed on program PODIS2 to convert the program to PODIS5. The entry points for these modifications are labeled 5a and 5b in Figure 2.

It is of interest to compare the calculated composition distribution curve (Figure 5) with the temperature rising elution fractionation (TREF) curve on linear low-density polyethylene.[38-41] The curves are somewhat similar in shape. Usami et al.[39] found two peaks in the TREF curve, a large peak at 90 °C associated with a low level of short chain branching and a broad peak at lower temperatures (ca. 70 °C) with higher levels of short-chain branching. One can readily associate the 90 °C TREF peak with component 3 (larger than 90 mol % ethylene) in Figure 5, and the low-temperature broad TREF peak with components 1 and 2 in Figure 5. The Gaussian broadening used in Figure 5 (though arbitrary) may reflect to some extent the separation mechanism in the TREF process.

IV. Perturbed Model and Process Heterogeneity.

A further refinement of the treatment is to introduce the perturbed model. Previously, the perturbed Markovian model was developed[1,2] and its use in the analysis of NMR data demonstrated. The perturbed model was found to be a good way to treat compositional heterogeneity under a number of conditions.

One of the ways the perturbation model can be especially useful is to treat process heterogeneity.[2] Variations in process parameters (temperature, feed rates, etc.) invariably show up as fluctuations in either reactivity ratios or monomer feed concentrations. These in turn show up as fluctuations in reaction probabilities. Using the error propagation treatment and mean deviations, we can derive the mean fluctuations in first-order Markovian probability, $\{P_{ij}\}$, e.g.

$$P_{ab} = \frac{1}{1 + r_a x}$$

$$\delta P_{ab} = \left| \frac{x}{(1 + r_a x)^2} \right| \delta r_a + \left| \frac{r_a}{(1 + r_a x)^2} \right| \delta x$$

where δP_{ij}, δr_i, and δx are the fluctuations due to reaction probabilities, reactivity ratios, and comonomer feed ratios, respectively.

In the perturbation treatment, we introduce a perturbation ϵ to the value P_{ij}, where $\epsilon \propto \delta P_{ij}$ in the case of process heterogeneity. Thus, instead of discrete reaction probabilities, we have a range of values that P_{ij} can assume. This procedure will, as expected, broaden the compositional distribution. A computer program that takes this effect into account is called PODIS5.

The modifications needed for the program PODIS5 are given in Figure 6. A third random number generator is used for the perturbation. Two methods to "smear out" P_{ij} can be done. One method is to use a rectangular function, $P_{ij} = P_{ij}{}^{\circ} \pm \epsilon$, where $P_{ij}{}^{\circ}$ is the probability in the absence of process heterogeneity. The second option is to

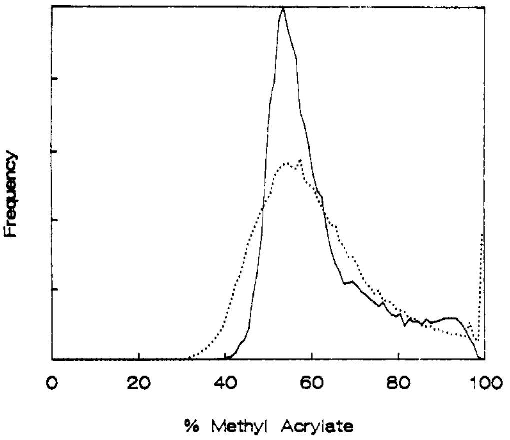

Figure 7. Predicted compositional distributions of a styrene/methyl acrylate copolymer. Solid line, distribution with no process heterogeneity (program PODIS3); dotted line, process heterogeneity added (Gaussian perturbation, $\epsilon = 0.1$, curve smoothed). Simulation was done through the program PODIS5.

use a Gaussian function g, with the standard deviation $\sigma = \epsilon\sqrt{3}$:

$$g(P_{ij}) = (2\pi\sigma^2)^{-1/2}\exp[-(P_{ij}-P_{ij}^\circ)^2/2\sigma^2]$$

In both cases, a random number in either the rectangular function or the Gaussian function[42] is taken and the procedure is the same as that adopted for the program PODIS3.

As an example, we can predict the compositional distribution of a styrene/methyl acrylate (S/MA) copolymer. Teramachi et al.[3] have determined the CCD of low-molecular-weight samples of this copolymer by a chromatographic cross-fractionation method. The appropriate parameters for sample L-SMA-87-B are given below:

reactivity ratios	feed composn, mol %	mol wt
$r_S = 0.68$	(S) = 32.9	$M_n = 1.0 \times 10^4$
$r_{MA} = 0.18$	(MA) = 67.1	$M_w = 1.5 \times 10^4$
conv = 86.7%		

The predicted CCD for this polymer in the batch copolymerization mode can be easily obtained through the program PODIS3. It is shown in Figure 7. This curve includes statistical and conversion heterogeneities and resembles the theoretical curve calculated from the theoretical expressions by Teramachi et al.[3] However, Teramachi's experimentally observed CCD is much broader. Teramachi et al.[3] had speculated on the source of the discrepancy: peak broadening in liquid chromatography, low reliability in the detection of MA, uncertainty in the calibration curve, and errant reactivity ratio values.

We believe an alternative interpretation of the broadened CCD is the fluctuation (perturbation) in the reaction probabilities. Taking an ϵ value of 0.10, we can readily obtain the compositional distribution as shown in Figure 7 through the program PODIS5. Indeed, the introduction of ϵ broadens the distribution. The agreement with the observed CCD is good.

V. Further Examples. To further illustrate the problem-solving ability of this present approach, we shall simulate three additional cases of the styrene/ethyl methacrylate copolymers. Earlier, Tacx et al.[6] have calculated the theoretical CCD's for several copolymers on the basis of statistical and conversion heterogeneity. In three cases studied (Figures 8 and 9 in ref 6), the observed CCD's do not fully match the experimentally determined CCD's. We shall introduce process heterogeneity and multistate heterogeneity, where necessary, and show compatibility with the observed CCD's using computer simulation.

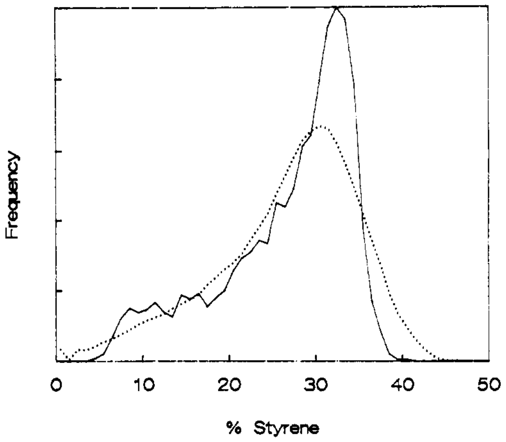

Figure 8. Simulated CCD of a styrene/ethyl methacrylate copolymer, case 1. Simulation was done through the program PODIS5. Solid line, $\epsilon = 0$; dotted line, $\epsilon = 0.04$ (Gaussian perturbation, curve smoothed).

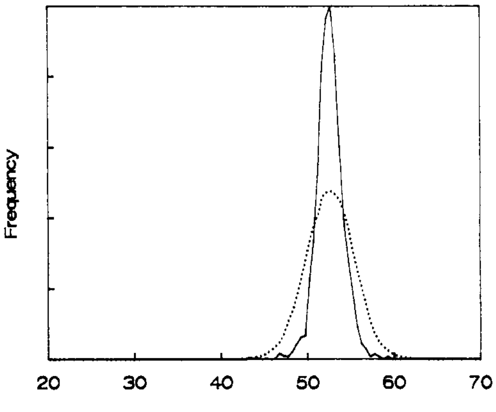

Figure 9. Simulated CCD of a styrene/ethyl methacrylate copolymer, case 2. Simulation was done through the program PODIS5. Solid line, $\epsilon = 0$; dotted line, $\epsilon = 0.03$ (Gaussian perturbation, curve smoothed).

The parameters used for the first two cases are given as follows:

Case 1. Bulk Copolymerization

reactivity ratio	feed composn, mol %	mol wt
$r_S = 0.46$	(S) = 24.6	not reported
$r_{EMA} = 0.38$	(EMA) = 75.4	(assume $M_n = 46\,000$ and $M_w = 92\,000$)
convn = 92%		

Case 2. Bulk Copolymerization

reactivity ratio	feed composn, mol %	mol wt
$r_S = 0.46$	(S) = 52.4	not reported
$r_{EMA} = 0.38$	(EMA) = 47.6	(assume $M_n = 46\,000$ and $M_w = 92\,000$)
convn = 92%		

In both cases, the reactivity ratios and the feed compositions used are taken directly from Tacx et al.[6] Computer simulation of the compositional distribution is straightforward. Using the program PODIS3, we can readily account for statistical and conversion heterogeneity; the simulated CCD's (solid lines) are given in Figure 8 and 9. The simulated curves have the same shapes as the theoretical curves obtained by Tacx et al.[6] As noted earlier, the experimentally observed curves are much broader in compositional spread. Since we expect more fluctuations in the kinetic parameters in bulk polymerization, we shall introduce a perturbation ($\epsilon = 0.03$–0.04) to the reaction probabilities. Computer simulation is carried out via the

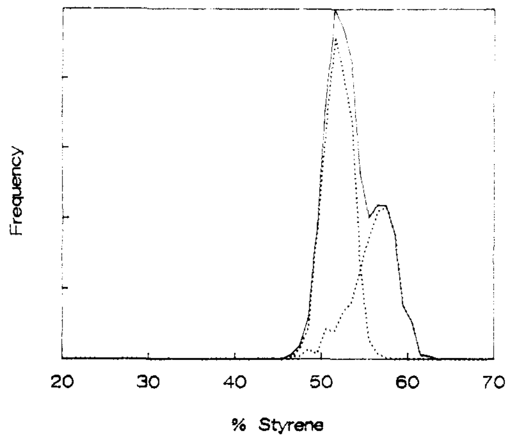

Figure 10. Simulated CCD of a styrene/ethyl methacrylate copolymer, case 3. Simulation was done through the program PODIS4. Two components are assumed. Solid line, overall composition; dotted lines, component compositions (component 1, 60%; component 2, 40%). Parameters are given in the text.

program PODIS5. The simulated CCD's (dotted lines) are now much closer to the observed CCD's in the extent of the compositional spread (Figures 8 and 9).

Note that in case 2 (Figure 9), although the shape of the simulated curve and the extent of the compositional spread are similar to the observed CCD, our simulated composition is centered on a styrene composition of 52.6 mol %. Curiously, the observed CCD[6] is centered on 58 mol % styrene. In order to shift the curve, we would need to make large changes in the reactivity ratios and/or the feed composition. We would then depart from the values reported earlier.[6] The nature of this discrepancy is not known.

The copolymer in case 3 was made with emulsion copolymerization. The observed CCD shows a bimodal distribution. In such a heterogeneous system it is possible that two kinds of copolymerization may be occurring with different reactivity ratios. This is a case of multistate heterogeneity. Through the use of two states, we can adequately simulate the observed CCD. After a few attempts, the parameters given below were chosen.

Case 3. Emulsion Copolymerization

Component 1. 60%

reactivity ratio	feed composn, mol %	mol wt
$r_S = 0.46$	(S) = 51.9	assume constant
$r_{EMA} = 0.38$	(EMA) = 48.1	46 000
convn = 92%		

Component 2. 40%

reactivity ratio	feed composn, mol %
$r_S = 0.59$	(S) = 54.9
$r_{EMA} = 0.27$	(EMA) = 45.1
convn = 92%	

The simulated CCD is shown in Figure 10. No perturbation (ϵ) has been used. The compatibility of the simulated curve with the reported CCD[6] strongly suggests that multistate heterogeneity is present in the copolymerization under consideration.

Note that the PODIS programs are proactive. The various parameters have been chosen to match the experimentally determined distributions. The programs are general and can be used either to fit the observed data or to predict the chemical composition distributions from known data on reactivity ratios and feed compositions (or, equivalently, from the reaction probabilities).

Conclusion

In this work we made a clear distinction among the four different kinds of compositional heterogeneity. We developed the PODIS family of programs to treat these different types of heterogeneity.

type	heterogeneity	program
1	statistical	PODIS2
2	conversion	PODIS3
3	multistate	PODIS4
4	process	PODIS5

Increasingly, techniques are being developed to measure compositional heterogeneity.[1–9,38–41] The use of this computer synthetic approach can help to elucidate the chemical composition distribution curves and understand the nature of compositional heterogeneity.

In the simulations carried out by the above programs, the following information is available: (1) the chemical composition distribution curve, (2) the second moment of the curve, (3) the average composition, (4) the average diad and triad sequence distributions. The relationship between the second moment (of the CCD) and the perturbation model has been previously described.[2] It may be noted that the diad and the triad sequences (as predicted by using the PODIS approaches) can be used to compare with observed NMR data. This comparison (i.e., analytical versus simulation approaches) is the subject for a future publication.[43]

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