Monte Carlo simulation of copolymerization and compositional inhomogeneity of copolymers: comparison to experimental data

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A review is given of the methods used to calculate copolymer composition as a function of chain length. A Monte Carlo simulation of copolymerization, which considers the initiation and propagation steps and yields cumulative copolymer composition as a function of chain length, is described in detail. The results of the simulations for three copolymer systems show that the initiation step significantly influences the short chains but its effect rapidly vanishes with increasing chain length. The results of the simulations for the three copolymer systems are compared to experimentally determined composition-chain length distributions. The agreement of the simulations and the experimental data is good for long chains but poor for short chains.

INTRODUCTION

The recognition of the polydispersity of chain lengths of polymers led to the theoretical prediction of such chain length distributions based on kinetic and statistical considerations. Subsequently, the recognition of the possibility of distributions of other variables such as branching, tacticity, geometrical isomerism, and copolymer composition has led to attempts to describe theoretically the superimposition of two or more of these distributions on the same polymer system. The experimental determination of the chain length distribution has been made convenient by such techniques as gel permeation chromatography (g.p.c.), and comparison to theoretical predictions is often easily accomplished. However, the theoretical description and experimental determination of the coupled distributions have been fraught with many difficulties. The state of this general problem has been recently reviewed by Mirabella and Johnson[1]. Further, the experimental determination of copolymer composition, as well as geometrical isomerism and addition variation in conjugated olefins as a function of molecular weight, has been investigated by Mirabella *et al.*[2–6].

The investigation of the coupling of the composition and chain length distributions of copolymers has been one of the most intense. Simha and Branson[7] and later Stockmayer[8] derived such distribution functions for copolymers. The results of Stockmayer[8] are most conveniently applied and can yield the overall distribution of compositions irrespective of chain length or the composition distribution at given finite chain length. However, these distributions are limited to 'instantaneous' copolymers, i.e. copolymers of very low conversion. It is important to recognize the difference between two types of compositional inhomogeneity. The so-called 'instantaneous' inhomogeneity occurs over an infinitesimal conversion increment and occurs in chains that are too short to be at statistical equilibrium. The so-called 'conversion' inhomogeneity occurs over large increments in conversion and is due to macroscopic variations in reaction parameters: in the simplest case, drift in monomer feed composition. Therefore, as pointed out by Stockmayer[8], the instantaneous composition distribution will often be insignificant compared to the composition distribution imposed on the system due to the steady change in monomer feed composition and, thus, mean copolymer composition. For the instantaneous copolymers the results of Stockmayer[8] indicate that (a) the compositions of a given chain length are normally distributed about the mean value with a standard deviation calculable from reaction parameters, and (b) the composition distribution broadens as chain length decreases.

Fueno and Furukawa[9] applied probability theory of Markov chains to derive equations which permit calculation of the copolymer composition as a function of chain length. They found, when only the initiation and propagation steps are considered, that as the chain length increases the effect of the initiation step rapidly vanishes and the composition distribution approaches its stationary value depending only on the probabilities governing the propagation step. The equations derived apply only to low conversion (instantaneous) copolymers since feed composition is assumed to remain constant.

The drift in cumulative composition as a function of conversion for high conversion copolymers can be obtained by employing the integrated copolymer equation as described by Skeist[10] and recast in a convenient form for analytical solution by Kruse[11]. However, the cumulative compositional spread obtained from the use of the integrated copolymer equation applies strictly to infinite chain length copolymer, only.

Thus the composition of high conversion copolymers as a function of finite chain length is not calculable from the above-mentioned theories. It is the intent of this paper to describe a Monte Carlo simulation of copolymerization which yields cumulative composition as a function of chain length for high conversion copolymers. The results of these calculations are compared to experimentally determined cumula-

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tive composition as a function of chain length for three high conversion copolymer systems.

The use of Monte Carlo simulation of copolymerization has been discussed in detail by Price[12] and applications of the technique have been described[13–17]. The advantage of the Monte Carlo simulation method is that a statistical sample of the copolymer sequences can be generated and approximate population values calculated from this sample. It is not necessary to generate all possible sequences as in exact enumeration techniques[18] which are exceedingly time-consuming and allow the examination of only short chains.

SIMULATION OF COPOLYMERIZATION

Mayo and Lewis[19] derived the well-known copolymer composition equation by considering four distinct propagation reactions:

$$\sim M_1^{\bullet} + M_1 \xrightarrow{k_{11}} \sim M_1^{\bullet} \quad (1)$$

$$\sim M_1^{\bullet} + M_2 \xrightarrow{k_{12}} \sim M_2^{\bullet} \quad (2)$$

$$\sim M_2^{\bullet} + M_1 \xrightarrow{k_{21}} \sim M_1^{\bullet} \quad (3)$$

$$\sim M_2^{\bullet} + M_2 \xrightarrow{k_{22}} \sim M_2^{\bullet} \quad (4)$$

These four processes can be considered as a first-order Markov chain, since the outcome of each event in the process is dependent only on the outcome of the preceding event[20]. By using the four rate constants, k_{ij}, and the molar concentrations of each monomer in the feed, C_1 and C_2, four conditional probabilities can be written describing processes (1) to (4), respectively, as follows:

$$P_{11} = \frac{k_{11}C_1}{k_{11}C_1 + k_{12}C_2} = \frac{1}{1 + C_2/r_1C_1} \quad (5)$$

$$P_{12} = \frac{k_{12}C_2}{k_{11}C_1 + k_{12}C_2} = \frac{1}{1 + r_1C_1/C_2} \quad (6)$$

$$P_{21} = \frac{k_{21}C_1}{k_{21}C_1 + k_{22}C_2} = \frac{1}{1 + r_2C_2/C_1} \quad (7)$$

$$P_{22} = \frac{k_{22}C_2}{k_{21}C_1 + k_{22}C_2} = \frac{1}{1 + C_1/r_2C_2} \quad (8)$$

where the usual 'ultimate unit' reactivity ratios, $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, are used. P_{ij} is the conditional probability that a chain ending in radical i adds monomer j. The probabilities can be calculated with the appropriate reactivity ratios and molar concentrations. In the Monte Carlo simulation, these probabilities are calculated before each event to be simulated and assigned to a proportionate interval between 0 and 1. A random number generator is then used to produce a number between 0 and 1. The outcome of the event is determined by comparing the magnitude of the random number to the appropriate intervals calculated from conditional probabilities (equations 5–8).

The initiation step was considered in this work. The first monomer unit of each chain was determined by calculating appropriate probabilities and comparing the magnitude of a random number to these. The initiation reactions, where I• is the initiator radical, can be written:

$$I^{\bullet} + M_1 \xrightarrow{k_{i1}} I - M_1^{\bullet} \quad (9)$$

$$I^{\bullet} + M_2 \xrightarrow{k_{i2}} I - M_2^{\bullet} \quad (10)$$

The initiation reactions are governed by the rate constants, k_{i1} and k_{i2}, which are rarely known. A reasonable assumption, which was made in this study, is that the initiator selects between monomers 1 and 2 only on the basis of feed composition and relative monomer reactivities toward the same radical. Thus, the probabilities of initiation for process 9 and 10, respectively, are:

$$P_{i1} = \frac{I_1C_1}{I_1C_1 + I_2C_2} \quad (11)$$

$$P_{i2} = \frac{I_2C_2}{I_1C_1 + I_2C_2} \quad (12)$$

where I_1 and I_2 refer to the relative reactivities of monomers 1 and 2, respectively, toward the same radical.

A computer program was written which incorporates the probabilities expressed in equations (5)–(8), (11) and (12) and permits computation of the instantaneous and cumulative copolymer composition for any desired chain length as a function of initial feed composition. The feed composition was varied sequentially and the instantaneous copolymer formed at each feed composition was accumulated with all previous instantaneous copolymers formed to yield the cumulative copolymer composition as a function of feed composition. The feed compositions were converted to molar conversions by calculating the feed-composition/conversion curve for the same copolymer systems. This was done by calculating the cumulative composition of the infinite molecular weight copolymer and feed composition as a function of conversion for these three systems using the equations of Kruse[11] and a probabilistic method as described by Harwood *et al.*[21–23]. Both procedures yield the same feed and copolymer-composition/conversion curves for the infinite molecular weight copolymer. All computing was done on a CDC 6600 computer.

The computer program which simulates copolymerization is listed in *Figure 1*. The procedure used was to compute the feed-composition/conversion curve as described above. This determined the direction of drift in feed composition as a function of conversion. Then 'ultimate' unit reactivity ratios, original feed mole fraction of monomer 1, chain length desired, increment in feed composition, a parameter which determines the frequency at which data is reported, a parameter indicating whether the feed composition of monomer 1 increases or decreases as a function of increasing conversion and relative reactivities of the monomers toward the radical were input to the computer program as indicated in statement 18 of *Figure 1*. Then the computer calculates the initiation probabilities and the conditional probabilities of propagation. The monomer chosen for initiation and then the sequence of monomer units up to the chain length desired were determined using these probabilities and the random number generator. The random number generator, RANF(O) (see *Figure 1*), was of the form[24]:

```
      PROGRAM MUNC(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C
C     THIS PROGRAM IS A MONTE CARLO SIMULATION OF COPOLYMERIZATION
C     FOR COPOLYMER CHAINS OF FINITE LENGTH==============================
C
      DIMENSION IDENT(8)
      DIMENSION M(75000)
      REAL M1REA,M2REA
  301 CONTINUF
      I=J=N=0
      SF2=P11=P22=P12=P21=MU=PTU=RNG=PI1=0.0
      R1=R2=SF1=DELF1=SAVP1=CPMM1=CPMM2=0.0
      READ(5,18)IDENT
   18 FORMAT(8A10)
      IF(EOF(5))300,82
   82 CONTINUE
      READ(5,1)R1,R2,SF1,N,DELF1,LC,IDOWN,M1REA,M2REA
1     FORMAT(3F10.5,I10,F10.5,I4,I2,2F5.1)
      WRITE(6,6)IDENT
   6  FORMAT(1H1,100(1H*),/,8A10,/,1H ,100(1H*)//)
      WRITE(6,123)M1REA,M2REA
  123 FORMAT(/1H ,*RELATIVE REACTIVITY OF MONOMER 1=*,F10.5,2X,
     1*RELATIVE REACTIVITY OF MONOMER 2=*,F10.5,/)
      WRITE(6,7)R1,R2,N,SF1,DELF1
   7  FORMAT(1H ,*R1=*,F10.5,2X,*R2=*,F10.5,2X,*STOCHASTIC CHAIN LENGTH=
     1*,I10,2X,*SMALL F1=*,F10.5,2X,*DFL SMALL F1=*,F10.5,//,1H ,100(1H*
     1),/)
      WRITE(6,8)
   8  FORMAT(1H ,*INSTANTANEOUS COPOLYMER COMPOSITION*,5X,*CUMULATIVE CO
     1POLYMER COMPOSITION*,6X,*FEED COMPOSITION*,
     1/,1H ,*MONOMER 1*,2X,*MONOMER 2*,20X,*MONOMER 1*,2X,*MONOMER 2*,
     118X,*MONOMER 1*,/,1H ,*MOLE PERC*,2X,*MOLE PERC*,20X,*MOLE PERC*,
     12X,*MOLE PERC*,18X,*MOLF FRAC*,/,1H ,100(1H*),///)
   80 CONTINUE
      STOR1=STOR2=0.0
      TOT=PMM1=PMM2=0.0
      I=1
      SF2=1.-SF1
C  CALCULATION OF CONDITIONAL PROBABILITIES
      P12=1./(1.+R1*(SF1/SF2))
      P11=1.-P12
      P21=1./(1.+R2*(SF2/SF1))
      P22=1.-P21
C     SET PROBABILITY FOR INITIATION
C     THE INITIATION STEP IS BASED ONLY ON FEED COMPOSITION
C  AND RELATIVE MONOMER REACTIVITIES TOWARD THE SAME RADICAL (M1REA
C  AND M2REA)
      PI1=(SF1*M1REA)/((SF1*M1REA)+((1-SF1)*M2REA))
      RNG=RANF(0)
      IF(RNG.LE.PI1)10,11
  10  MU=1
      STOR1=1.0
      GO TO 2
  11  MU=2
      STOR2=1.0
  2   M(I)=MU
      I=I+1
C  TEST FOR THE CHAIN LENGTH REQUESTED
      IF(I-1.EQ.N)100,3
C  DETERMINATION OF MONOMER TO BE ADDED IN THE PROPAGATION STEP
  3   IF(MU.EQ.1)12,13
  12  PTU=P11
      GO TO 4
  13  PTU=P22
      GO TO 5
  4   RNG=RANF(0)
      IF(RNG.LE.PTU)14,15
  5   RNG=RANF(0)
      IF(RNG.LE.PTU)16,17
  14  MU=1
      STOR1=STOR1+1.0
      GO TO 2
  15  MU=2
      STOR2=STOR2+1.0
      GO TO 2
  16  MU=2
      STOR2=STOR2+1.0
      GO TO 2
  17  MU=1
      STOR1=STOR1+1.0
      GO TO 2
  100 CONTINUE
C  CALCULATION OF INSTANTANEOUS COPOLYMER COMPOSITION
      TOT=STOR1+STOR2
      PMM1=STOR1*100.0/TOT
      PMM2=100.0-PMM1
C  CALCULATION OF CUMULATIVE COPOLYMER COMPOSITION
      J=J+1
      SAVP1=PMM1+SAVP1
      CPMM1=SAVP1/J
      CPMM2=100.00-CPMM1
C  TEST TO DETERMINE FREQUENCY AT WHICH DATA IS TO BE REPORTED
      IF(((J-1)/LC)*LC.NE.(J-1))GO TO 102
      WRITE(6,81)PMM1,PMM2,CPMM1,CPMM2,SF1
   81 FORMAT(1H ,F10.5,1X,F10.5,19X,F10.5,1X,F10.5,17X,F10.5)
  102 CONTINUE
C  INCREMENT IN FEED COMPOSITION AND TEST FOR MONOMER DEPLETION
      SF1=SF1-DELF1
      IF(IDOWN)152,152,151
  152 CONTINUE
      IF(1.0-SF1)200,200,80
  151 CONTINUF
      IF(SF1)200,200,80
  200 CONTINUE
      WRITE(6,87)PMM1,PMM2,CPMM1,CPMM2,SF1,J
   87 FORMAT(1H ,F10.5,1X,F10.5,19X,F10.5,1X,F10.5,17X,F10.5,//,1H ,*J=*
     1,I10)
      GO TO 301
  300 CONTINUE
      STOP
      END
```

Figure 1 Computer program used to simulate initiation and propagation in binary copolymerization by the Monte Carlo method

Table 1 Output from the computer program in *Figure 1*. J is the total number of chains 'grown' in simulation. Relative reactivity of monomer 1 = 1.00000; relative reactivity of monomer 2 = 1.00000; r_1 = 68.00000; r_2 = 0.01000; stochastic chain length = 50; small F_1 = 0.90000; del small F_1 = 0.00010

Instantaneous copolymer composition		Cumulative copolymer composition		Feed composition
Monomer 1 (mol %)	Monomer 2 (mol %)	Monomer 1 (mol %)	Monomer 2 (mol %)	Monomer 1 (mol fraction)
100.00000	0.00000	100.00000	0.00000	0.90000
100.00000	0.00000	99.51697	0.48303	0.85000
98.00000	2.00000	99.46454	0.53546	0.80000
96.00000	4.00000	99.37508	0.62492	0.75000
100.00000	0.00000	99.22739	0.77261	0.70000
100.00000	0.00000	99.09556	0.90444	0.65000
100.00000	0.00000	98.97168	1.02832	0.60000
98.00000	2.00000	98.84262	1.15738	0.55000
98.00000	2.00000	98.70832	1.29168	0.50000
98.00000	2.00000	98.55365	1.44635	0.45000
94.00000	6.00000	98.39112	1.60888	0.40000
96.00000	4.00000	98.21014	1.78986	0.35000
96.00000	4.00000	98.00800	1.99200	0.30000
96.00000	4.00000	97.75788	2.24212	0.25000
88.00000	12.00000	97.47008	2.52992	0.20000
94.00000	6.00000	97.12198	2.87802	0.15000
90.00000	10.00000	96.61442	3.38558	0.10000
76.00000	24.00000	95.83625	4.16375	0.05000
2.00000	98.00000	93.78489	6.21511	0.00000

J = 9000

Table 2 Reaction parameters for three styrene vinyl stearate copolymers
Reactivity ratios[25]: r_1 = 68, styrene = monomer 1; r_2 = 0.01, vinyl stearate = monomer 2

Sample number	Original feed composition (mol fraction vinyl stearate)	Mol % conversion*	Overall composition (mol % styrene)†‡
422-103-1	0.10	94.2	94.40
422-103-2	0.20	70.5	92.79
422-103-5	0.50	36.7	97.43

* All copolymerizations done in bulk at 60°C for 72 h. Copolymerizations 1 and 2 were run uninterrupted with 0.2 mol % azobisisobutyronitrile (AIBN). Copolymerization 5 was run for 24 h with 0.2 mol % AIBN and then interrupted, another 0.2 mol % AIBN added and continued. Weight conversions in ref 4 have been converted to molar conversions.

† Based on carbon–hydrogen analysis with oxygen obtained by difference.

‡ Residual monomer was extracted from the copolymers with portions (5 to 1 based on polymer) of methanol at the boiling point for 1 h until an aliquot of methanol failed to produce turbidity when added to water, indicating the absence of monomer. Four or more extractions were done on each copolymer sample

$$X_{i+1} = aX_i \pmod{2^b} \tag{13}$$

where mod2^b represents a remaindering function. The random number generator, RANF(O), generates a uniform distribution of random numbers between 0 and 1. The length of the period of the sequence of random numbers was calculated to be 2.81×10^{14}. Since the largest number of statistical trials performed for any one copolymer simulation was less than 7 million, it was certain that a non-repeating series of random numbers was used in each simulation. The computer output is a report of reaction parameters, stochastic chain length, feed composition and instantaneous and cumulative copolymer composition, as shown in *Table 1*. The actual sequence of monomer units along the instantaneous copolymer chains can be printed out to visualize the stochastic selection process. The reaction parameters for the three poly(styrene-co-vinyl stearate) copolymer systems, which were experimentally analysed for composition as a function of molecular weight, previously[4], and simulated in this work, are shown in *Table 2*.

The Monte Carlo simulations were done identically for corresponding chain lengths of each sample in *Table 2*. *Table 3* lists the mole fractional increments in feed composition used for each stochastic chain length of all three samples. Simulations were run from the original feed composition in styrene listed in *Table 2* down to one mole fractional feed increment unit above zero styrene mole fraction in the feed. Each copolymer system simulation was done at least three times at varying increments and agreement between corresponding results was excellent in all cases. This agreement was due to the small increments in feed mole fraction employed as stochastic chain length decreased. Larger increments were employed and found to give unreproducible results for the short stochastic chains (especially chains of DP = 10).

RESULTS AND DISCUSSION

The Monte Carlo simulations were done assuming that styrene and vinyl stearate had equal reactivities toward the initiator, and then assuming that styrene had a relative reactivity of 50 and vinyl stearate a relative reactivity of 1 toward the initiator, based on relative reactivities of these monomers with another radical[26]. *Table 4* shows the cumulative copolymer composition (F_1) as a function of chain length (DP) for these two initiation models. It is apparent that when styrene was assumed to be 50 times as reactive with the initiator as vinyl stearate little variation in F_1 as a function of DP was observed. However, when equal reactivities were assumed, a significant variation in F_1 as a function of DP was observed. Thus, only the initiation model assuming equal reactivity will be considered hereafter.

The cumulative mole fractions of styrene in the three styrene/vinyl stearate copolymers for various degrees of

Table 3 Monte Carlo simulation parameters for poly(styrene-co-vinyl stearate). Samples 422-103-1, 422-103-2, and 422-103-5

Increment in feed mole fraction employed	Length of stochastic chain
0.02	75 000
0.01	75 000
0.02	10 000
0.01	10 000
0.005	5 000
0.000 1	5 000
0.005	1 000
0.000 1	1 000
0.005	500
0.000 1	500
0.005	100
0.000 1	100
0.005	50
0.000 1	50
0.005	10
0.000 1	10
0.000 01	10

Table 4 Cumulative copolymer composition as a function of chain length for two initiation models (see equation 11)

Chain length (*DP*)	Sample 422-103-1 p(molar) = 0.942		Sample 422-103-2 p(molar) = 0.706		Sample 422-103-5 p(molar) = 0.367	
	$P_{i1}=\frac{50X_1}{50X_1+X_2}$	$P_{i1}=X_1$	$P_{i1}=\frac{50X_1}{50X_1+X_2}$	$P_{i1}=X_1$	$P_{i1}=\frac{50X_1}{50X_1+X_2}$	$P_{i1}=X_1$
	F_1	F_1	F_1	F_1	F_1	F_1
10	0.9251	0.8788	0.9876	0.9450	0.9705	0.9280
50	0.9258	0.9165	0.9874	0.9790	0.9731	0.9630
100	0.9262	0.9216	0.9873	0.9840	0.9734	0.9700
500	0.9270	0.9260	0.9873	0.9880	0.9730	0.9750
1 000	0.9270	0.9260	0.9872	0.9880	0.9727	0.9750
5 000	–	0.9270	–	0.9880	–	0.9750
10 000	–	0.9270	–	0.9880	–	0.9750
75 000	–	0.9270	–	0.9880	–	0.9750

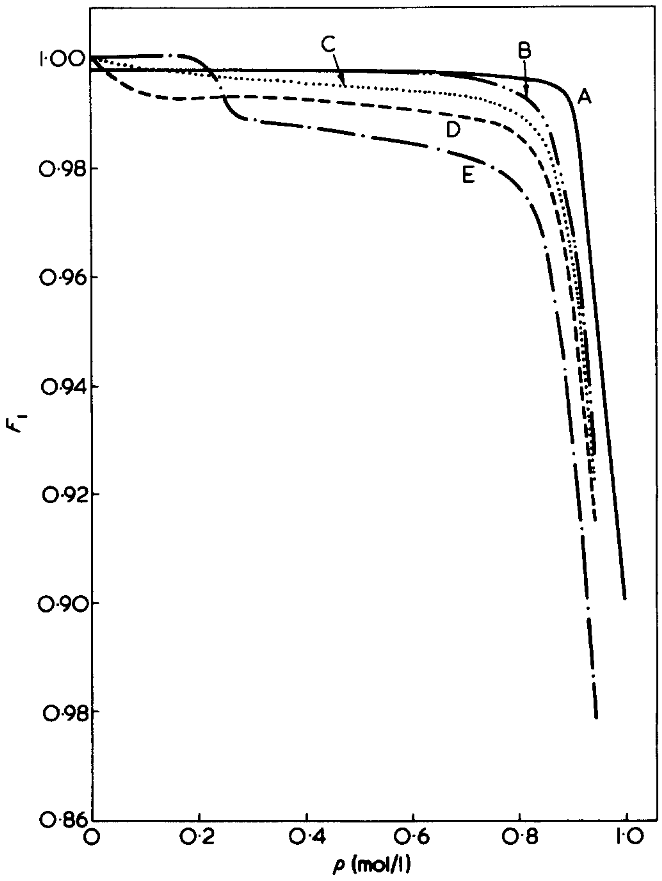

Figure 2 Cumulative mole fraction (F_1) of styrene in sample 422-103-1, f_{10} = 0.900 of poly(styrene-co-vinyl stearate) *versus* molar conversion (p). The original mole fraction of monomer 1 in the feed is designated f_{10}. A, $N = \infty$; B, $N \geq 500$; C, $N = 100$; D, $N = 50$; E, $N = 10$

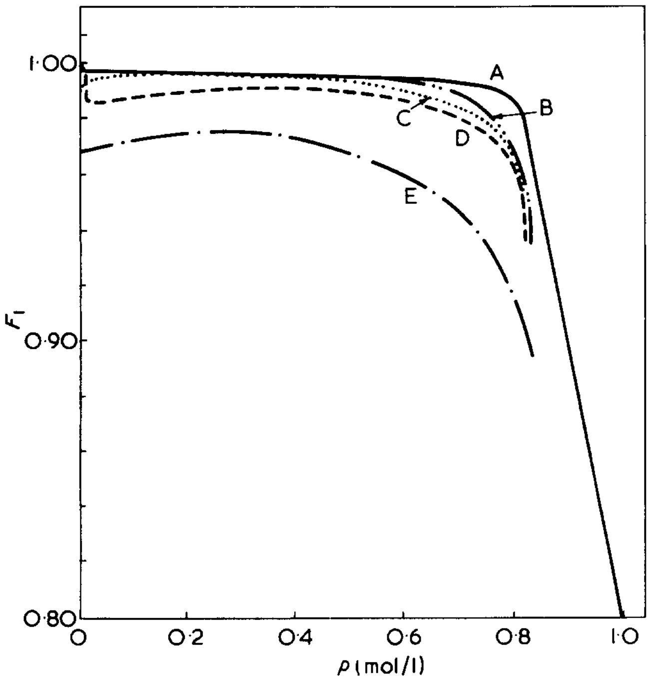

Figure 3 Cumulative mole fraction (F_1) of styrene in sample 422-103-2, f_{10} = 0.800 of poly(styrene-co-vinyl stearate) *versus* molar conversion (p). The original mole fraction of monomer 1 in the feed is designated f_{10}. A, $N = \infty$; B, $N \geq 500$; C, $N = 100$; D, $N = 50$; E, $N = 10$

polymerization (*DP*) as a function of molar conversion (p) determined from the Monte Carlo simulations are plotted in *Figures 2–4*. The cumulative mole fraction of styrene as a function of *DP* was determined experimentally, previously[4]. The theoretical cumulative mole fraction of styrene as a function of *DP* was determined from *Figures 2–4* by reading off the styrene mole fraction for each *DP* at any desired conversion. *Figures 5–7* show the theoretical and experimental mole fraction styrene in the copolymer *versus* log *DP* curves for samples 422-103-1, 422-103-2 and 422-103-5, respectively, where the theoretical curves were determined at experimental conversions shown in *Table 2*.

Figures 5–7 show that the theoretical drift in composition with chain length is qualitatively similar but quantitatively much less than observed experimentally. The agreement of theory and experiment is good for chains longer than about 300 (>log 2.5) units but rapidly becomes poorer for shorter chains. The distribution of compositions indicates that these systems are polyblends, consisting of a high *DP* portion of copolymer with high styrene content and a low *DP* portion of copolymer with high vinyl stearate content. The gel permeation chromatograms[4], in fact, showed that each system had a bimodal molecular weight distribution. The short chains were apparently formed by some process not included in the Monte Carlo simulations.

The results of these Monte Carlo simulations, when the initiation and propagation steps were considered, for the cumulative high conversion copolymers are similar to the

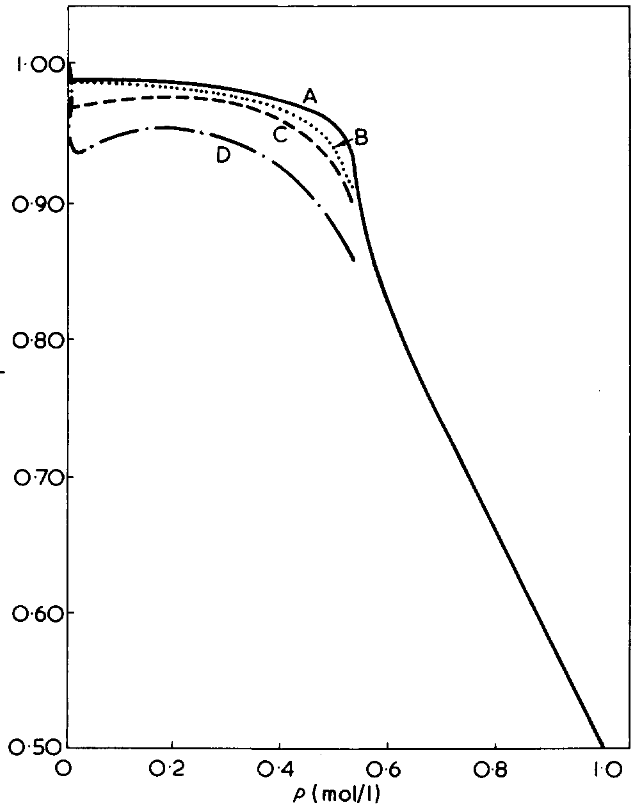

Figure 4 Cumulative mole fraction (F_1) of styrene in sample 422-103-5, f_{10} = 0.500 of poly(styrene-co-vinyl stearate) *versus* molar conversion (p). The original mole fraction of monomer 1 in the feed is designated f_{10}. A, $N = \infty$; B, $N \geq 100$; C, $N = 50$; D, $N = 10$

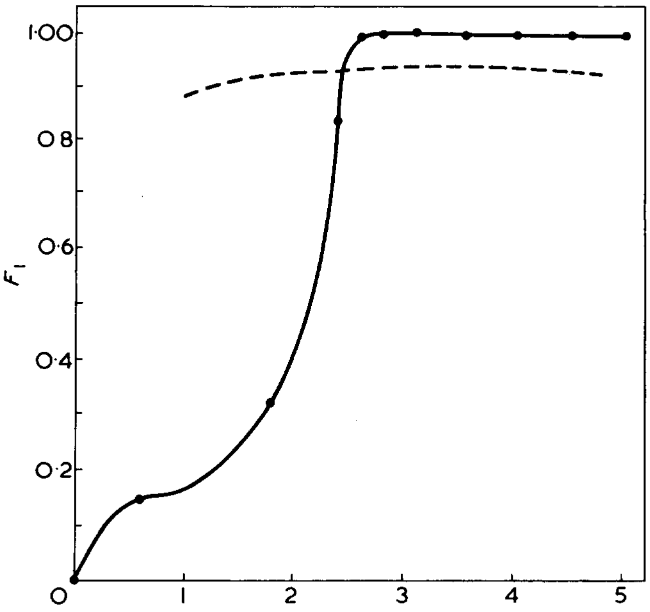

Figure 5 Cumulative mole fraction (F_1) of styrene in sample 422-103-1, f_{10} = 0.900 of poly(styrene-co-vinyl stearate) *versus* the log of the degree of polymerization (DP). The original mole fraction of monomer 1 in the feed is designated f_{10}. ———, Experiment; – – – –, theory

results of Fueno and Furukawa[9] for very low conversion copolymers, when the initiation and propagation steps were also considered. In both studies the effect of the initiation step was largest for short chains and rapidly vanished for long chains. It is apparent from the experimental curves in *Figures 5–7* that the effect of the initiation step, assuming equal reactivity of each monomer with the initiation, was not sufficient to explain the enrichment of the short chains with vinyl stearate. As shown in *Table 2*, these copolymers were thoroughly extracted with methanol so that it is doubtful that this effect was due to residual vinyl stearate monomer.

In order to determine the proportion of polymer which

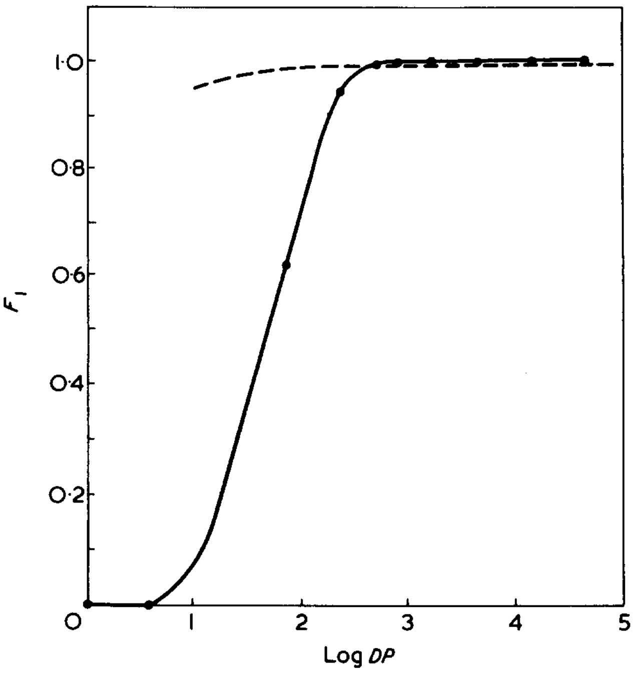

Figure 6 Cumulative mole fraction (F_1) of styrene in sample 422-103-2, f_{10} = 0.800 of poly(styrene-co-vinyl stearate) *versus* the log of the degree of polymerization (DP). The original mole fraction of monomer 1 in the feed is designated f_{10}. ———, Experiment; – – – –, theory

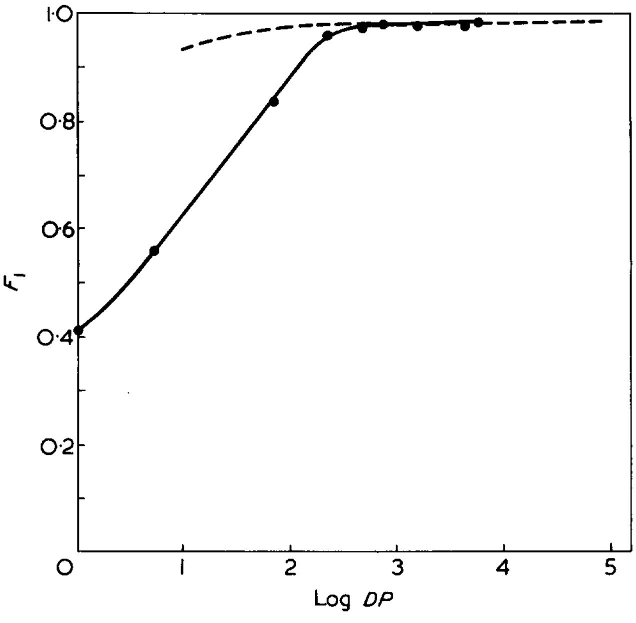

Figure 7 Cumulative mole fraction (F_1) of styrene in sample 422-103-5, f_{10} = 0.500 of poly(styrene-co-vinyl stearate) *versus* the log of the degree of polymerization (DP). The original mole fraction of monomer 1 in the feed is designated f_{10}. ———, Experiment; – – – –, theory

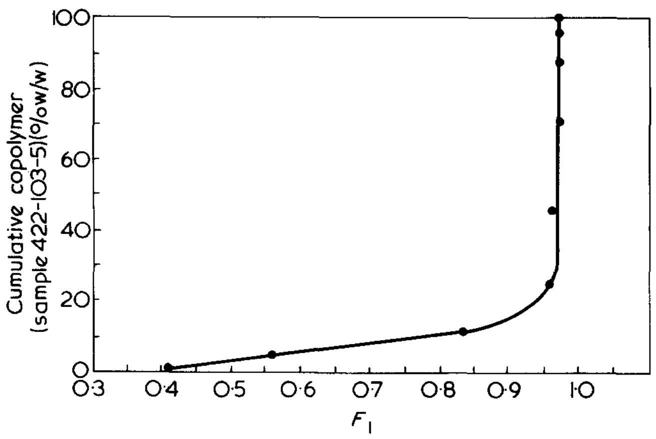

Figure 8 Cumulative wt % of copolymer in sample 422-103-5 of poly(styrene-co-vinyl stearate) *versus* cumulative mole fraction (F_1) of styrene in the copolymer

varied significantly from the calculated compositional range, the cumulative weight percent of copolymer versus mole fraction styrene in the copolymer was determined experimentally for sample 422-103-5 and is shown in *Figure 8*. *Figure 7* shows that the predicted composition range for this sample was from 0.928 to 0.975 mole fraction styrene and *Figure 8* shows that about 20% (w/w) of the copolymer is out of this range. Thus, a significant portion of copolymer was not contained within the calculated compositional range, and these low *DP* chains make up a significant part of the whole copolymer.

CONCLUSIONS

Monte Carlo simulation of copolymerization permits the realistic prediction of the cumulative copolymer composition as a function of *DP*. The effect of the initiation step was shown to be significant for the chains of low *DP* in this study. A knowledge of the initiation rate constants would be desirable when comparing simulations to experimental results. Apparently, the short chains investigated in this study were influenced by a more dramatic effect than the initiation step considered herein, as seen in the experimental data presented in *Figure 5–7*. If other phenomena, such as phase heterogeneity during the bulk copolymerization, are operative, large increases in compositional heterogeneity might result. However, such effects would be quite difficult to include in the simulation. The termination step might also be expected to contribute toward broader compositional heterogeneity, especially for short chains. Inclusion of the termination step, as well as the initiation step, would require an expansion of the method used to calculate cumulative composition, since copolymer chains would have to be sorted on the basis of *DP* as they terminated. This would require considerably more computer space and time if the total number of chains simulated for each sample was similar to that employed in this study.

The study demonstrates the applicability of the Monte Carlo method to the prediction of cumulative or instantaneous composition of high conversion copolymers as a function of *DP*. Further comparisons of this method to experimental data may aid in the understanding of the interplay of events in the growth of a real copolymer chain from initiation to termination.

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