Monte Carlo simulation of terpolymerization

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A simulation of terpolymerization, using the Monte Carlo method, and a computer program which performs the calculations for finite and infinite chain length conditions, are described. Terpolymer composition and sequence distributions are given as a function of chain length for two terpolymer systems. It was found that statistical equilibrium is achieved at chain lengths of about 100 units.

INTRODUCTION

In a previous paper[1] a Monte Carlo simulation of copolymerization was described. The present paper describes a Monte Carlo simulation of terpolymerization. Little work has been done on the simulation of the stochastic growth of terpolymers. In this work the initiation and the propagation steps were included in a model which simulates the growth of terpolymer chains of any arbitrarily specified length. A computer program was used to calculate terpolymer compositions and monomer sequence distributions for finite chain length terpolymers, by the Monte Carlo method, and for infinite chain length terpolymers, by the usual probabilistic method[2,3].

SIMULATION OF TERPOLYMERIZATION

Three distinct initiation reactions are needed to describe the initiation of the termonomers (M_1, M_2 and M_3) in a terpolymerization, assuming one initiation species (I·):

$$I\cdot + M_1 \xrightarrow{k_{i1}} I - M_1\cdot \quad (1)$$

$$I\cdot + M_2 \xrightarrow{k_{i2}} I - M_2\cdot \quad (2)$$

$$I\cdot + M_3 \xrightarrow{k_{i3}} I - M_3\cdot \quad (3)$$

where the initiation rate constants are k_{i1}, k_{i2} and k_{i3}. The initiation rate constants are rarely known. The assumption made in this work was that the initiator selects between monomers 1, 2 and 3 only on the basis of feed composition and relative monomer reactivities toward the same radical. Thus, the initiation probabilities for processes (1) to (3), respectively, are given by:

$$P_{i1} = \frac{I_1C_1}{I_1C_1 + I_2C_2 + I_3C_3} \quad (4)$$

$$P_{i2} = \frac{I_2C_2}{I_1C_1 + I_2C_2 + I_3C_3} \quad (5)$$

$$P_{i3} = \frac{I_3C_3}{I_1C_1 + I_2C_1 + I_3C_3} \quad (6)$$

where I_1, I_2 and I_3 refer to the normalized relative reactivities of monomers 1, 2 and 3, respectively, toward the same radical and, similarly, C_1, C_2 and C_3 are the molar concentrations of the monomers in the feed. There are nine propagation reactions which need to be considered in order to describe the terpolymerization propagation steps, assuming that the ultimate unit of a 'living' polymer chain solely determines which monomer unit is added next[4]. These nine propagation reactions lead to six 'ultimate unit' reactivity ratios[4] and nine conditional probability expressions:

$$P_{11} = \frac{1}{1 + \frac{C_2}{r_{12}C_1} + \frac{C_3}{r_{13}C_1}} \quad (7)$$

$$P_{12} = \frac{1}{1 + \frac{r_{12}C_1}{C_2} + \frac{r_{12}C_3}{r_{13}C_2}} \quad (8)$$

$$P_{13} = \frac{1}{1 + \frac{r_{13}C_1}{C_3} + \frac{r_{13}C_2}{r_{12}C_3}} \quad (9)$$

$$P_{21} = \frac{1}{1 + \frac{r_{21}C_2}{C_1} + \frac{r_{21}C_3}{r_{23}C_1}} \quad (10)$$

$$P_{22} = \frac{1}{1 + \frac{C_1}{r_{21}C_2} + \frac{C_3}{r_{23}C_2}} \quad (11)$$

$$P_{23} = \frac{1}{1 + \frac{r_{23}C_1}{r_{21}C_3} + \frac{r_{23}C_2}{C_3}} \quad (12)$$

$$P_{31} = \frac{1}{1 + \frac{r_{31}C_2}{r_{32}C_1} + \frac{r_{31}C_3}{C_1}} \quad (13)$$

Table 1 Constants used for the styrene/butadiene/methyl methacrylate and styrene/vinyl acetate/methyl acrylate systems

Monomer number	Monomer	Original feed composition		Normalized relative reactivity of monomer with styrene radical*†	Reactivity ratios‡	
		Mol %	W %			
1	Styrene	33.33	40.31	$l_1 = 0.2381$	$r_{12} = 0.825$	$r_{13} = 0.485$
2	Butadiene	33.33	20.94	$l_2 = 0.3095$	$r_{21} = 1.39$	$r_{23} = 0.75$
3	Methyl methacrylate	33.33	38.75	$l_3 = 0.4524$	$r_{31} = 0.422$	$r_{32} = 0.25$
1	Styrene	33.33	37.59	$l_1 = 0.4310$	$r_{12} = 6.5$	$r_{13} = 0.75$
2	Vinyl acetate	33.33	31.16	$l_2 = 0.0086$	$r_{21} = 0.15$	$r_{23} = 0.03$
3	Methyl acrylate	33.33	31.15	$l_3 = 0.5604$	$r_{31} = 0.18$	$r_{32} = 6.3$

* See equations (4)–(6). † Values were calculated by normalizing the values given in ref 6 for each set of three monomers. ‡ Values obtained from ref 7

$$P_{32} = \frac{1}{1 + \frac{r_{32}C_1}{r_{31}C_2} + \frac{r_{32}C_3}{C_2}} \quad (14)$$

$$P_{33} = \frac{1}{1 + \frac{C_1}{r_{31}C_3} + \frac{C_2}{r_{32}C_3}} \quad (15)$$

where each probability, P_{jk}, refers to a chain ending in monomer j adding monomer k, and the reactivity ratios, r_{jk}, are numbered as is customary[5]. The sum of each set of three equations (4) to (6), (7) to (9), (10) to (12), and (13) to (15) is unity.

In the Monte Carlo simulation these probabilities are calculated before each event (using the current values of feed composition and the various constants involved) and assigned a proportionate interval between 0 and 1, as described previously[1]. A random number generator is then used to produce uniformly distributed random numbers which determine the outcome of each initiation and propagation event[1]. A computer program was used to perform these calculations and to compute instantaneous and cumulative terpolymer compositions and monomer sequence distributions. The probabilities expressed in equations (7) to (15) were also used to compute the previously mentioned quantities for the infinite chain length terpolymers by the usual probabilistic method[2,3]. All computing was done on a CDC 175 computer. A listing of the FORTRAN 4 extended program is available on request.

The Monte Carlo simulation was performed for the terpolymer systems styrene/butadiene/methyl methacrylate (S/B/MMA) and styrene/vinyl acetate/methyl acrylate (S/VA/MA). The simulations were done for chains from 10 to 5000 units long and for infinite chain length. The simulations were done from zero conversion up to the desired conversion in 0.5% molar conversion increments. Thus, in the case of the S/B/MMA system, the growth of 170 chains was simulated from 0 to 85% molar conversion and in the case of the S/VA/MA system the growth of 150 chains was simulated from 0 to 75% molar conversion, at each chain length. *Table 1* gives the values of the constants used. The normalized relative reactivities of the monomers were calculated using values of the relative reactivities of the monomers with the styrene radical[6]*.

RESULTS AND DISCUSSION

Tables 2 and *3* present the results of the Monte Carlo simulations for the two terpolymer systems, mentioned previously. These data show that as the chain length increases the effect of the initiation step vanishes and statistical equilibrium is approached. At chain lengths of about 100 units and greater, the agreement between composition and sequence distribution data obtained by simulation and infinite chain length data becomes good. This is similar to previous results in which agreement between copolymer simulation data and experimental data became good at chain lengths of about 300 units and greater[1].

CONCLUSIONS

Monte Carlo simulation of terpolymerization can aid in visualizing this extremely complex process. The ability of the model used in the simulation to predict the composition and monomer sequence distributions of chains of finite length depends on whether the model includes the major governing factors of the polymerization. Further study is necessary in order to improve the Monte Carlo simulation of terpolymerization by comparing data from simple simulation models to experimental data and then modifying the models as indicated by the comparison.

* This choice was made because of available data. Relative reactivities with highly electrophilic initiator radicals could be quite different.

Table 2 Composition and sequence distribution data as a function of chain length for the styrene/butadiene/methyl methacrylate system

Chain length	Conversion (mol %)	Cumulative terpolymer composition (wt %)			Sequence distribution		
		A-styrene	B-butadiene	C-methyl methacrylate	Diads (number fraction of all diads)		Triads (number fraction of all triads)
10	85.0	36.313	22.242	41.444	AA = 0.0703	BB = 0.1006	AAA = 0.0214 ABA = 0.0259 ACA = 0.0577
					AB = 0.1893	BC = 0.3156	AAB = 0.0259 ABB = 0.0510 ACB = 0.1169
					AC = 0.2663	CC = 0.0579	AAC = 0.0703 ABC = 0.0865 ACC = 0.0311
							BAB = 0.0392 BBB = 0.0259 BCB = 0.0769
							BAC = 0.0865 BBC = 0.0984 BCC = 0.0481
							CAC = 0.0562 CBC = 0.0688 CCC = 0.0133
50	85.0	37.486	21.875	40.639	AA = 0.0811	BB = 0.1031	AAA = 0.0210 ABA = 0.0221 ACA = 0.0556
					AB = 0.1734	BC = 0.3131	AAB = 0.0443 ABB = 0.0500 ACB = 0.1292
					AC = 0.2822	CC = 0.0470	AAC = 0.0754 ABC = 0.0794 ACC = 0.0394
							BAB = 0.0256 BBB = 0.0311 BCB = 0.0703
							BAC = 0.0795 BBC = 0.0950 BCC = 0.0413
							CAC = 0.0645 CBC = 0.0696 CCC = 0.0065
100	85.0	37.893	21.854	40.253	AA = 0.0848	BB = 0.1021	AAA = 0.0245 ABA = 0.0198 ACA = 0.0574
					AB = 0.1714	BC = 0.3157	AAB = 0.0435 ABB = 0.0507 ACB = 0.1280
					AC = 0.2808	CC = 0.0452	AAC = 0.0769 ABC = 0.0808 ACC = 0.0376
							BAB = 0.0250 BBB = 0.0296 BCB = 0.0723
							BAC = 0.0781 BBC = 0.0953 BCC = 0.0426
							CAC = 0.0629 CBC = 0.0699 CCC = 0.0053
500	85.0	37.539	22.342	40.119	AA = 0.0833	BB = 0.1051	AAA = 0.0231 ABA = 0.0216 ACA = 0.0550
					AB = 0.1749	BC = 0.3186	AAB = 0.0467 ABB = 0.0515 ACB = 0.1267
					AC = 0.2727	CC = 0.0455	AAC = 0.0737 ABC = 0.0803 ACC = 0.0359
							BAB = 0.0250 BBB = 0.0324 BCB = 0.0744
							BAC = 0.0782 BBC = 0.0937 BCC = 0.0430
							CAC = 0.0604 CBC = 0.0723 CCC = 0.0060
1000	85.0	37.588	22.217	40.195	AA = 0.0838	BB = 0.1045	AAA = 0.0229 ABA = 0.0218 ACA = 0.0533
					AB = 0.1734	BC = 0.3179	AAB = 0.0462 ABB = 0.0508 ACB = 0.1266
					AC = 0.2743	CC = 0.0461	AAC = 0.0755 ABC = 0.0790 ACC = 0.0371
							BAB = 0.0248 BBB = 0.0319 BCB = 0.0743
							BAC = 0.0776 BBC = 0.0945 BCC = 0.0427
							CAC = 0.0606 CBC = 0.0722 CCC = 0.0062
5000	85.0	37.573	22.312	40.115	AA = 0.0845	BB = 0.1052	AAA = 0.0235 ABA = 0.0213 ACA = 0.0550
					AB = 0.1731	BC = 0.3193	AAB = 0.0471 ABB = 0.0514 ACB = 0.1266
					AC = 0.2726	CC = 0.0454	AAC = 0.0748 ABC = 0.0791 ACC = 0.0359
							BAB = 0.0242 BBB = 0.0316 BCB = 0.0749
							BAC = 0.0776 BBC = 0.0959 BCC = 0.0427
							CAC = 0.0601 CBC = 0.0722 CCC = 0.0061
∞	85.0	37.581	22.313	40.106	AA = 0.0844	BB = 0.1050	AAA = 0.0234 ABA = 0.0214 ACA = 0.0547
					AB = 0.1736	BC = 0.3191	AAB = 0.0472 ABB = 0.0514 ACB = 0.1267
					AC = 0.2723	CC = 0.0455	AAC = 0.0746 ABC = 0.0791 ACC = 0.0362
							BAB = 0.0244 BBB = 0.0315 BCB = 0.0748
							BAC = 0.0775 BBC = 0.0954 BCC = 0.0426
							CAC = 0.0601 CBC = 0.0722 CCC = 0.0060

Table 3 Composition and sequence distribution data as a function of chain length for the styrene/vinyl acetate/methyl acrylate system

Chain length	Conversion (mol %)	Cumulative terpolymer composition (wt %)			Sequence distribution								
		A, styrene	B, vinyl acetate	C, methyl acrylate	Diads (number fraction of all diads)			Triads (number fraction of all triads)					
10	75.0	47.939	10.462	41.599	AA = 0.1268	BB = 0.0127		AAA = 0.0386	ABA = 0.0076	ACA = 0.1762			
					AB = 0.0708	BC = 0.1387		AAB = 0.0168	ABB = 0.0076	ACB = 0.0747			
					AC = 0.5533	CC = 0.0977		AAC = 0.1611	ABC = 0.0478	ACC = 0.1149			
								BAB = 0.0008	BBB = 0.0025	BCB = 0.0176			
								BAC = 0.0562	BBC = 0.0134	BCC = 0.0252			
								CAC = 0.1737	CBC = 0.0428	CCC = 0.0227			
50	75.0	48.635	11.320	40.045	AA = 0.1327	BB = 0.0142		AAA = 0.0414	ABA = 0.0073	ACA = 0.1806			
					AB = 0.0736	BC = 0.1470		AAB = 0.0194	ABB = 0.0052	ACB = 0.0730			
					AC = 0.5435	CC = 0.0890		AAC = 0.1639	ABC = 0.0537	ACC = 0.1037			
								BAB = 0.0015	BBB = 0.0029	BCB = 0.0207			
								BAC = 0.0515	BBC = 0.0180	BCC = 0.0329			
								CAC = 0.1658	CBC = 0.0383	CCC = 0.0201			
100	75.0	49.246	10.835	39.919	AA = 0.1374	BB = 0.0140		AAA = 0.0440	ABA = 0.0050	ACA = 0.1850			
					AB = 0.0672	BC = 0.1425		AAB = 0.0174	ABB = 0.0053	ACB = 0.0726			
					AC = 0.5499	CC = 0.0889		AAC = 0.1695	ABC = 0.0520	ACC = 0.1055			
								BAB = 0.0015	BBB = 0.0023	BCB = 0.0175			
								BAC = 0.0473	BBC = 0.0181	BCC = 0.0342			
								CAC = 0.1672	CBC = 0.0367	CCC = 0.0190			
500	75.0	49.268	10.816	39.916	AA = 0.1387	BB = 0.0133		AAA = 0.0462	ABA = 0.0056	ACA = 0.1855			
					AB = 0.0655	BC = 0.1446		AAB = 0.0167	ABB = 0.0047	ACB = 0.0711			
					AC = 0.5482	CC = 0.0897		AAC = 0.1684	ABC = 0.0496	ACC = 0.1058			
								BAB = 0.0016	BBB = 0.0024	BCB = 0.0193			
								BAC = 0.0455	BBC = 0.0171	BCC = 0.0349			
								CAC = 0.1673	CBC = 0.0391	CCC = 0.0193			
1000	75.0	49.319	11.027	39.654	AA = 0.1398	BB = 0.0143		AAA = 0.0469	ABA = 0.0060	ACA = 0.1833			
					AB = 0.0678	BC = 0.1449		AAB = 0.0180	ABB = 0.0051	ACB = 0.0719			
					AC = 0.5445	CC = 0.0887		AAC = 0.1679	ABC = 0.0507	ACC = 0.1058			
								BAB = 0.0017	BBB = 0.0027	BCB = 0.0190			
								BAC = 0.0464	BBC = 0.0181	BCC = 0.0349			
								CAC = 0.1652	CBC = 0.0381	CCC = 0.0184			
5000	75.0	49.359	10.974	39.667	AA = 0.1399	BB = 0.0140		AAA = 0.0470	ABA = 0.0059	ACA = 0.1844			
					AB = 0.0672	BC = 0.1448		AAB = 0.0177	ABB = 0.0049	ACB = 0.0719			
					AC = 0.5454	CC = 0.0887		AAC = 0.1680	ABC = 0.0506	ACC = 0.1047			
								BAB = 0.0016	BBB = 0.0026	BCB = 0.0193			
								BAC = 0.0464	BBC = 0.0180	BCC = 0.0343			
								CAC = 0.1655	CBC = 0.0381	CCC = 0.0192			
∞	75.0	49.371	10.990	39.639	AA = 0.1396	BB = 0.0140		AAA = 0.0467	ABA = 0.0059	ACA = 0.1846			
					AB = 0.0676	BC = 0.1445		AAB = 0.0177	ABB = 0.0049	ACB = 0.0719			
					AC = 0.5458	CC = 0.0883		AAC = 0.1679	ABC = 0.0507	ACC = 0.1044			
								BAB = 0.0016	BBB = 0.0027	BCB = 0.0191			
								BAC = 0.0466	BBC = 0.0177	BCC = 0.0342			
								CAC = 0.1655	CBC = 0.0379	CCC = 0.0189			

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