

# Sequence length distribution in vinyl copolymers using a Monte Carlo simulation method

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A simulation of the copolymerization of vinyl monomers has been made, based on the assumption that the propagation step is a first order Markov process. The simulation aims at determining the copolymer sequence length distribution either in the form of mole fraction of monomer units of type 1 or 2 within segments of  $n$  consecutive units of either monomer 1 or 2 as a function of  $n$ , or in the form of fractions of different diads, triads, tetrads, etc. for any value of the fractional conversion. Statistical evaluation of the simulation as well as comparison with theoretical data and nuclear magnetic resonance data show that the simulation affords suitable sequence length distribution information when the initial propagation probability pairs ( $P_{11}$ ,  $P_{22}$ ) are not very dissimilar.

(Keywords: copolymerization; sequence length distribution, Monte Carlo simulation; nuclear magnetic resonance)

## INTRODUCTION

The application of the Monte Carlo simulation method (MSM) to first order Markov processes like polycondensation and polymerization of vinyl monomers is not a new technique to model changes in the polymer behaviour during the course of reaction. An examination of the relevant literature on the subject discloses the major aspects of interest with regard to the use of MSM in copolymers. Thus, Kumskov and Yufenov<sup>1</sup> used this method to model the synthesis of phenolformaldehyde copolymers. Cooper *et al.*<sup>2-5</sup> applied it to polyurethane block copolymers aiming at determining compositional heterogeneities, sequence and molecular weight distributions and premature phase separation. This method has also been used to calculate monomer reactivity ratios in vinyl copolymerization<sup>6,7</sup>, to establish the effects of depropagation on the kinetics of vinyl polymerization<sup>8-11</sup>, to evaluate compositional heterogeneity in low molecular weight copolymers<sup>12,13</sup>, to simulate the crystallization of copolymers<sup>14</sup> and the structure of copolymers in solution<sup>15-17</sup> and to rationalize the adsorption behaviour of random copolymers of vinyl acetate and ethylene on silica surfaces<sup>18</sup>. Very surprisingly, however, only few authors have used the MSM to determine sequence length distributions (SLDs) in copolymers<sup>19,20</sup>.

Over the last 20 years, copolymers have been a major subject of research in our laboratory. SLD data of the copolymers synthesized by us therefore represent very valuable information for the rationalization of ultimate copolymer properties, namely water uptake in hydrogels and their elastic behaviour<sup>21-25</sup>. Our interest in SLD, and the lack of work in this field, prompted us to develop a simulation capable of providing reliable SLD data.

Furthermore, it must be recalled that it is not possible to obtain theoretically an overall distribution of  $n$ -mers as a function of  $n$  for any value of the fractional conversion ( $\theta$ )<sup>25</sup>, whereas in principle, a Monte Carlo simulation could easily provide it.

It is our intention in this paper to compare SLD information calculated by means of a computer program based on MSM concepts with SLD data obtained via nuclear magnetic resonance (n.m.r.) spectra of copolymers. By achieving this main aim, the reliability of the MSM will also be examined.

## GENERATION OF A COPOLYMER MOLECULE VIA A MONTE CARLO SIMULATION

### *Preliminary considerations*

Before starting the design of this computer program, a few conceptual decisions had to be made. Firstly one must consider the termination step in the simulation. This step undoubtedly affects the composition of the individual macromolecules within the same sample and the molecular weight distribution (MWD) of the system under consideration. However, its effect on the overall SLD is questionable. On the other hand, to evade the termination step represents an interesting conceptual problem cleverly brought up by Wittmer and Schmitt<sup>26</sup>. These authors state that the type of compositional inhomogeneity found in a polyreaction with monomer addition and chain termination (free-radical polymerization) is conceptually different from that found for polyreactions without chain termination (living polymerization). For the first type of polyreaction, they point out that every individual polymer molecule shows a 'fingerprint' which reveals the degree of conversion at which it was formed due to the smaller lifetime of the growing chain in comparison with the total time of reaction. For a living polymerization, on the other hand,

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every polymer molecule represents along its chain the course of the polymer reaction. The compositional inhomogeneity for this case has been defined as 'chemical inhomogeneity of the second type'. Apart from this conceptual problem, it is reasonable to expect that overall SLD to be independent of the type of compositional inhomogeneity and therefore, for the sake of simplification, evade the termination step. However, the importance of this step must be emphasized when simulations of the MWD are to be made<sup>12</sup>.

The second decision concerns whether a single chain or few chains should be produced simultaneously. This point is important when the reliability of the simulation is tested<sup>26</sup>. However, the simultaneous generation of more than one chain requires the use of a larger computer memory space which would not allow one to build molecules of high enough degree of polymerization (DP); according to Marabella<sup>27</sup>, the MSM only affords a realistic prediction of the copolymer cumulative composition when the DP exceeds 1000 monomer units.

The penultimate point to take into account is the initiation step. It has been shown that the effect of this step on the copolymer composition vanishes as long as the DP increases<sup>27,28</sup>. Furthermore, the cross-propagation reaction in the early stages of the polymerization diminishes the importance of the initiation step. However, for the sake of completeness, the simulation used here comprises a procedure based on Marabella's earlier considerations<sup>27</sup>, namely that the probabilities of initiation via a process initiator/monomer 1 ( $P_{i1}$ ) or a process initiator/monomer 2 ( $P_{i2}$ ) are:

$$P_{i1} = \frac{I_1 C_1}{I_1 C_1 + I_2 C_2} \quad (1)$$

$$P_{i2} = \frac{I_2 C_2}{I_1 C_1 + I_2 C_2} \quad (2)$$

Assuming that  $I_1 = I_2$ ,  $P_{i1}$  and  $P_{i2}$  become the feed mole fractions. The first monomer in the chain is selected from the feed mixture by comparing  $P_{i1}$  and  $P_{i2}$  with a random number. The details of the actual simulation are given in the next section and consequently no further comments will be given here. The case of radiation-initiated polymerization is considered here only when both monomers are equally amenable to double bond opening via radiation, that is, when the initiation step is controlled by the feed composition.

Finally, with regard to the propagation step, four processes are considered as a first order Markov chain, that is, the addition of a new monomer to the chain only depends on the last monomer added to the chain. The classical expressions for the cross-propagation probabilities are<sup>29</sup>:

$$P_{11} = \frac{r_1 C_1}{r_1 C_1 + C_2} \quad (3)$$

$$P_{12} = 1 - P_{11} \quad (4)$$

$$P_{22} = \frac{r_2 C_2}{C_1 + r_2 C_2} \quad (5)$$

$$P_{21} = 1 - P_{22} \quad (6)$$

In equations (3) and (5),  $r_1$  and  $r_2$  are the usual first order Markov reactivity ratios.

In summary, the simulation used in this work considers

the initiation step although in a simplified manner, generates a single high DP chain and evades the termination step. The term first order Markov process refers entirely to the propagation step of the copolymerization.

Figure 1 shows the flow diagram of the computer program used here. The data input takes the form of feed mole composition of monomer 1 ( $f_1$ ), reactivity ratios of monomers 1 and 2 ( $r_1, r_2$ ), number of feed molecules ( $N$ ) and the required degree of conversion ( $\theta_f$ ). Once the initiation has taken place and  $f_1$  and  $P_{ij}$  ( $i, j=1$  or  $2$ ) have been recalculated accounting for this addition, the program identifies the monomer added and, depending on the answer, activates one propagation procedure or the other. The conditional statements for each addition procedure are given in Figure 1.

Once the next monomer is added to the stochastic chain,  $f_i$  and  $P_{ij}$  are recalculated and the current conversion  $\theta$  is compared with the required one  $\theta_f$ . If the former is smaller than the latter, the proper propagation procedure is activated again. This loop is repeated until  $\theta = \theta_f$ . At this stage, the program proceeds to perform the SLD calculations as well as the instantaneous and

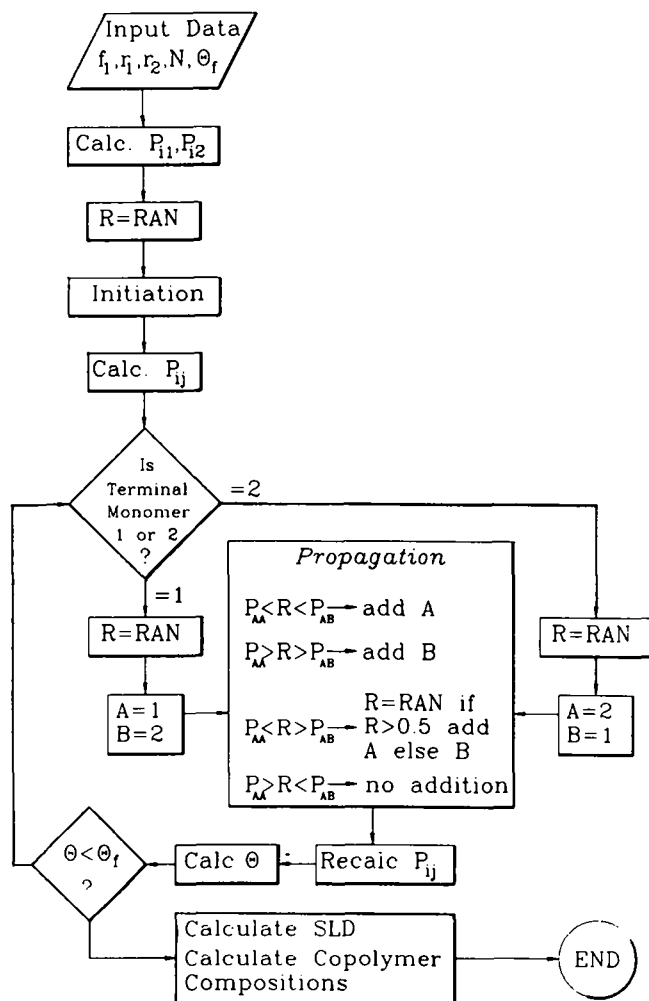


Figure 1 Flow diagram of the simulation program. The letters A and B are defined as monomers 1 or 2 depending on the last monomer added. Thus, if terminal monomer is 1, A = 1 and B = 2 and if terminal monomer is 2, A = 2 and B = 1. If the random number RAN generated is  $P_{AA} < R > P_{BB}$ , the program generates another RAN. If the latter is bigger than 0.5 the program adds an A unit to the stochastic chain and B if it is smaller than 0.5

cumulative copolymer composition determinations as a function of  $\theta$ .

From the considerations given above it follows that the nature of the random number generator is important<sup>30</sup>. The random number generator used in this simulation is a system-supplied linear congruential generator based in the recurrence relation:

$$K_{j+1} = aK_j + c \quad (7)$$

The sequence of numbers ( $K_j$ ) generated by the random number generator has a period of  $2^{32}$ . The starting seed is initiated every time the program is invoked. The program has been performed on an IBM computer in Turbo Pascal language (Borland, Version 5.5).

Two types of SLD are calculated from the high DP stochastic chain: (i) mole fraction of monomer units of type 1 or 2 within segments of  $n$  consecutive units of either monomer 1 or 2 ( $f_{in}$ ) ( $0 < n < DP$ ) as a function of  $n$ ; and (ii) normalized fraction of diads (AA, BB, AB and BA), normalized fractions of triads (AAA, AAB, ABA, BAA, ABB, BAB, BBA and BBB) and normalized fraction of tetrads (AAAA, AAAB, AABA, ..., BBBB) in the copolymer. The evaluation of this latter type of SLD is necessary in order to compare the stochastic SLD and those obtained by n.m.r. The program has also been implemented with procedures for the calculation of the copolymer cumulative composition and the instantaneous copolymer composition. For the latter, the following expression has been used<sup>31</sup>:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (8)$$

The cumulative copolymer composition is readily calculated by using counters for monomers 1 and 2 added to the copolymer and total number of molecules added at any stage of conversion.

The total number of feed molecules ( $N$ ) requires further comment, given in the next section. The program is currently being extended to the calculation of SLD in terpolymers.

#### Test of the reliability of the simulation

The stability of the probabilities given by equations (3) to (6) is very dependent on the initial total number of molecules  $N$  in the feed. Consequently, before one may proceed further, the lowest number of feed molecules that provides stable distributions must be determined. This has been done by generating stochastic chains under the same feed mole fraction, reactivity ratios and fractional conversion and changing  $N$  from 1000 to 60 000. The constant conditions selected were:  $f_1 = 0.5$ ,  $r_1 = r_2 = 1$  and fractional conversion  $\theta_f = 0.1$ . This selection of input parameters is dictated by the following arguments: (i)  $r_1 r_2 = 1$  and therefore the copolymerization is perfectly random; and (ii) the feed mole fraction and reactivity ratios chosen give rise to an azeotropic copolymerization (instantaneous feed and copolymer composition are the same at any stage of conversion). This allows one to use low conversions (0.1) for this test of reliability without affecting the final result. Accordingly, for these conditions the distributions calculated will only depend on  $N$  and therefore this quantity can be established.

Three stochastic chains have been produced for every  $N$  value in three separate experiments and their SLDs have been calculated. The similarity of two distributions

can be determined by means of the chi-square test<sup>32</sup>:

$$\chi^2 = \sum_i \frac{(R_i + S_i)^2}{R_i + S_i} \quad (9)$$

where  $R_i$  and  $S_i$  are the  $i$ th values of the two sets of distributions. Of course, the larger the value of  $\chi^2$ , the higher the dissimilarity of both distributions. The three SLD obtained for each value of  $N$  have been compared by means of equation (9) and mean  $\chi^2$  values ( $\langle \chi^2 \rangle$ ) have been calculated. The results are shown in Figure 2 where the variation of  $\langle \chi^2 \rangle$  for the SLD of monomer 2 is represented as a function of  $N$ . The insert gives the SLD of monomer 2 for three  $N$  values (1000, 5000 and 30 000). It is apparent from this figure that: (i) a minimum  $N$  value of 30 000 is required in order to get the lowest  $\langle \chi^2 \rangle$  values and therefore more stable SLD; (ii) the insert shows that the SLDs are influenced by  $N$ . Accordingly, a value of  $N = 30 000$  will be used hereafter. This value, furthermore, provides  $DP > 1000$  even at very low conversions ( $\theta_f = 0.05$ ) and hence realistic predictions of the copolymer cumulative composition can be expected<sup>27</sup>.

The first reliability test to be performed once  $N$  has been established concerns the copolymer composition  $\langle C_c \rangle$  at low values of the fractional conversion ( $\theta_f = 0.05$ ) and for different feed mole compositions ( $f_1$ ). Low  $\theta_f$  values are required since clearly the higher the conversion, the better the agreement between the real and the calculated  $\langle C_c \rangle$  value. The conditions selected to determine the reliability of  $\langle C_c \rangle$  data obtained via the MSM are: (i)  $r_1 = r_2 = 1$ ; (ii)  $N = 30 000$ ; and (iii)  $\theta_f = 0.05$  (as above). The results obtained are given in Figure 3a where  $\langle C_c \rangle$  is plotted against  $f_1$ .

Under these conditions the diagonal in Figure 3a represents the expected values whereas the points are 'experimental' values (mean values of 10 separate experiments; the standard deviations are in all cases lower than 0.01). The simulation therefore only provides accurate

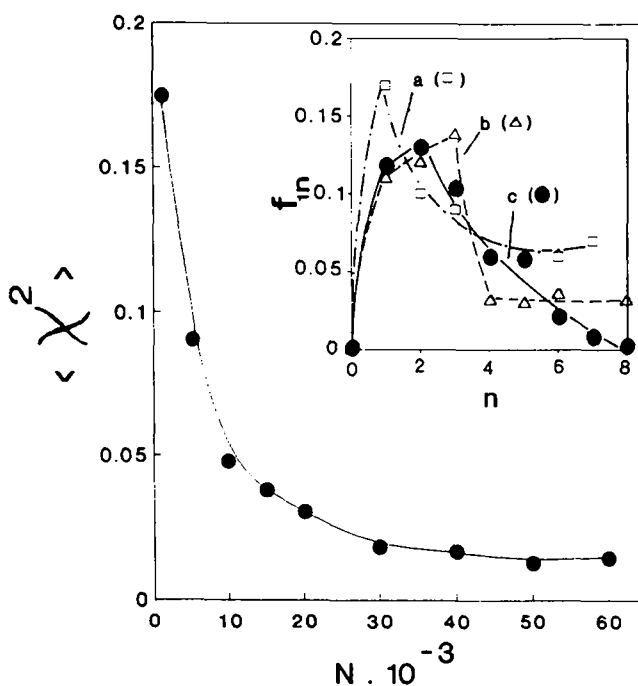
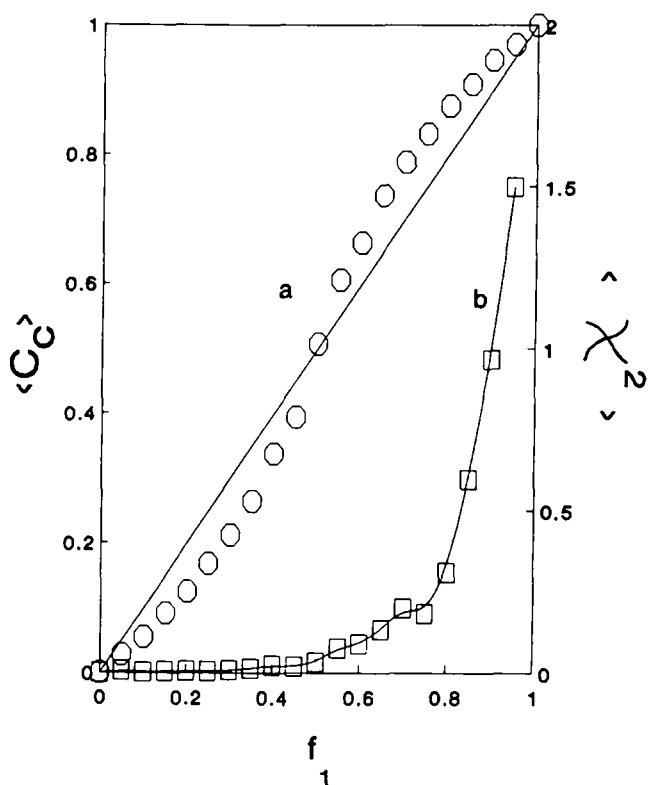


Figure 2 Variation of  $\langle \chi^2 \rangle$  for the distributions of monomer 2 as a function of the initial total of molecules in the feed  $N$ . Insert shows SLD obtained for (a)  $N = 1000$ ; (b)  $N = 5000$  and (c)  $N = 30 000$



**Figure 3** (a) Mean mole composition of the stochastic chain  $\langle C_c \rangle$  against feed mole composition. Input parameters used in the simulation:  $r_1=r_2=1$ ;  $N=30000$  and  $\theta=0.05$ . (b) Change of  $\langle \chi^2 \rangle$  with  $f_1$  for monomer 1

values of  $\langle C_c \rangle$  when  $f_1$  is close to 0.5 and hence when the initial probabilities  $P_{ii}$  ( $i=1$  or  $2$ ) are close to 0.5 (since under these conditions  $f_i=P_{ii}$ ). The differences found, however, are not prohibitively high and can be considered as experimental error. Similar behaviour has been reported elsewhere<sup>7</sup>.

Figure 3b shows the variation of  $\langle \chi^2 \rangle$  (obtained from the comparison of three distributions for each feed composition) as a function of  $f_1$  for monomer 1 (the behaviour associated with monomer 2 is the mirror image of that given in Figure 2b for monomer 1). For  $f_1$  values greater than 0.7, the SLD of the stochastic chains undergoes important changes from one experiment to another. In other words, the increase in compositional inhomogeneity produces less consistent simulated SLD (this is also expected in real samples).

A last test of the MSM of copolymerization made here involves the comparison of the instantaneous composition ( $F_1$ ) data as a function of  $\theta$  obtained by this method and those obtained by means of the Skeist equation<sup>33</sup> and equation (8):

$$\ln(1-\theta) = \int \frac{df_1}{(F_1-f_1)} \quad (10)$$

Equation (10) allows one to calculate  $\chi^2$  when  $f_1$  changes during this conversion from  $f_{1i}$  to  $f_{1j}$ . For convenience the integral form of equation (10) has been used here<sup>34</sup>:

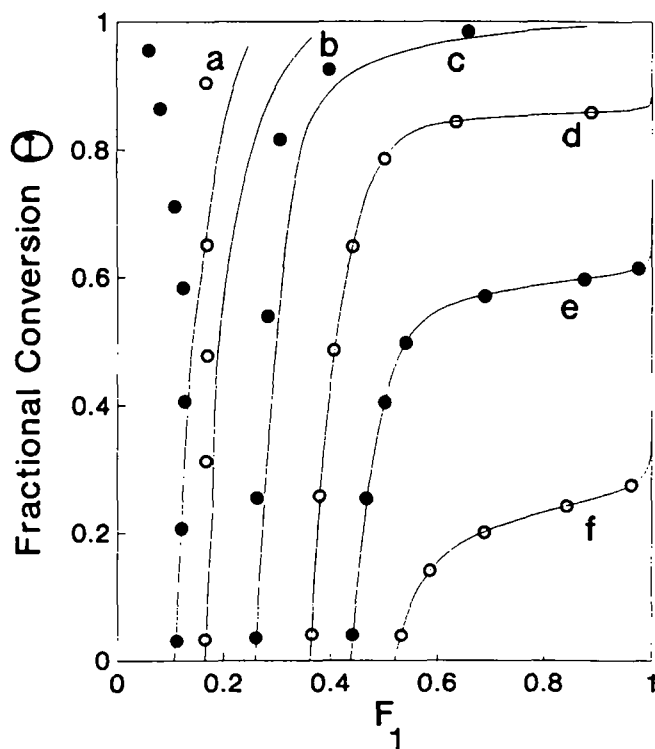
$$\theta = 1 - \left( \frac{f_{1j}}{f_{1i}} \right)^\alpha \left( \frac{1-f_{1j}}{1-f_{1i}} \right)^\beta \left( \frac{f_{1i}-\delta}{f_{1j}-\delta} \right)^\gamma \quad (11)$$

where

$$\alpha = \frac{r_2}{(1-r_2)}, \beta = \frac{r_1}{(1-r_1)}, \gamma = \frac{(1-r_1r_2)}{(1-r_1)(1-r_2)}, \delta = \frac{(1-r_2)}{(2-r_1-r_2)}$$

This comparison is aimed at establishing whether the copolymerization simulation affords the same compositional drifting behaviour as that obtained by means of the theoretical approach (equation (11) in conjunction with equation (8)). The system chosen for this comparison is one which has recently been studied extensively: *N*-vinyl-2-pyrrolidone (VP)(monomer 1)/butyl acrylate (BA)(monomer 2) for which the reactivity ratios<sup>21</sup> are:  $r_1=0.02$  and  $r_2=0.8$ . The selection of this system is dictated by its fractional conversion–instantaneous copolymer composition ( $\theta-F_1$ ) behaviour, namely the presence of an azeotropic composition at  $f_1=0.165$  and the existence of increasing compositional drift as a function of  $f_1$  for values of this quantity higher than the azeotropic composition<sup>21</sup>. The results are given in Figure 4, where the solid lines represent the values obtained by the MSM, whereas the points were calculated via the theoretical approach. As can be observed from this figure, both methods provide the same ( $\theta-F_1$ ) behaviour for  $f_1 > 0.3$ . For  $f_1 < 0.3$ , however, the variation of  $F_1$  with  $\theta$  obtained by means of the MSM departs from the behaviour found using the theoretical approach. The reason for this departure can be ascribed to the initial propagation probabilities. The corresponding ( $P_{11}, P_{22}$ ) pairs for the  $f_1$  values used here are:  $f_1=0.1$ : (0.0022, 0.878);  $f_1=0.165$ : (0.039, 0.802);  $f_1=0.3$ : (0.079, 0.651);  $f_1=0.5$ : (0.167, 0.444);  $f_1=0.7$ : (0.318, 0.255) and  $f_1=0.9$ : (0.474, 0.082). Clearly, therefore, the MSM does not afford reliable ( $\theta-F_1$ ) data when one of the starting probabilities is very small ( $P_{ii} < 0.08$ ) and simultaneously the other one is very big ( $P_{jj} > 0.7$ ).

In summary, the preliminary tests of the copolymerization simulation based on the MSM reveal that: (i)  $N$



**Figure 4** Fractional conversion ( $\theta$ ) as a function of the instantaneous copolymer composition ( $F_1$ ) for the following different  $f_1$  values: (a) 0.1; (b) 0.165; (c) 0.3; (d) 0.5; (e) 0.7 and (f) 0.9. Solid lines represent data obtained by MSM whereas the points have been calculated via the theoretical approach (equation (11) in conjunction with equation (8))

must be  $>30000$  in order to obtain reliable SLD data; (ii) the  $\langle C_c \rangle$  values calculated via the simulation at low conversions depart from the experimental values when the initial  $(P_{11}, P_{12})$  pairs are very dissimilar; (iii) the MS does not afford reliable  $(\theta - F_1)$  data when one of the initial probabilities is very small and, simultaneously, the other one is very big.

#### COMPARISON OF SLD DATA OBTAINED VIA MSM AND NMR

The structure of copolymers is a topic of major interest to polymer scientists. There are many papers devoted to the evaluation of SLD data via n.m.r. spectroscopy. However, few of them can be used here since not all provide the necessary input data, mainly feed compositions and fractional conversions. Among those suitable for comparison, a few have been rejected due to the unreliability of data (ethylene sulphide (ES)/iso-butylene sulphide (IBS))<sup>35</sup>, insufficient experimental data (acrylonitrile (AN)/butadiene (BU))<sup>36</sup>, unreliable presentation of data (recasting in form of fraction of triads produces negative values) (styrene/methyl methacrylate)<sup>37</sup> and non-existence of real experimental data (styrene/methyl acrylate)<sup>38</sup>.

However, five systems fulfil the necessary requirements. The comonomer pairs listed as monomer-1/monomer-2 are:

1. AN/vinyl chloride (VC)<sup>39</sup>
2. VC/isobutylene (IB)<sup>40</sup>
3. VC/vinyl acetate (VA)<sup>41</sup>
4. ES/propylene sulphide (PS)<sup>35</sup>
5. PS/IBS<sup>35</sup>

The SLD data obtained for systems 1 and 2 have been evaluated from low conversion samples ( $0.05 < \theta_f < 0.1$ ) and consequently experimental and calculated SLD values will be compared graphically (Figures 5 and 6 respectively). However, the SLD data provided for systems 3, 4 and 5 have been determined from low and high conversion samples and therefore the comparison between experimental and calculated values is given in tabular form (Tables 1, 2 and 3 respectively).

Figure 5 shows the diad distribution (experimental and calculated) for the system AN/VC. Not surprisingly, the experimental values and those obtained via the MSM fit reasonably well for  $0.15 < f_1 < 0.8$ . Higher and lower values of  $f_1$  give rise to an overestimate of the like-like diads (11 or 22). As before, this behaviour may be ascribed to the initial probability pairs  $(P_{11}, P_{22})$  which are:  $f_1 = 0.13$ : (0.11, 0.78) and  $f_1 = 0.8$ : (0.76, 0.12), that is, simultaneously, one initial probability is very big and the other one very small.

The system VC/IB has been considered here due to the fact that the experimental values of diads and tetrads cannot be explained by the copolymerization theory based on the terminal model<sup>40</sup> but requires the penultimate effect to be taken into consideration. Accordingly, the MSM must be expected to produce diad data which do not fit the experimental values, since the simulation made here is based on the assumption that the propagation is a first order Markov process. Figure 6 shows the disagreement between the calculated and experimental values, although it should be noted that the overall trends are similar.

Finally, Tables 1, 2 and 3 provide SLD for another

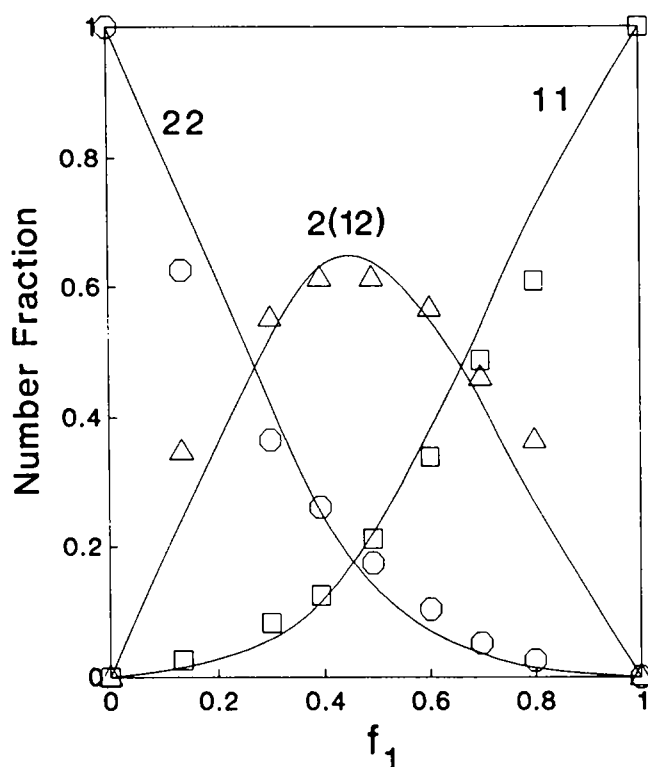


Figure 5 Diad distribution (11, 22 and 12) of AN(1)/VC(2) copolymers as a function of  $f_1$ . The curve for the distribution of diads 12 is actually the summation of equal number fraction of 12 and 21 diads. Continuous curve is theoretical; symbols are experimental values

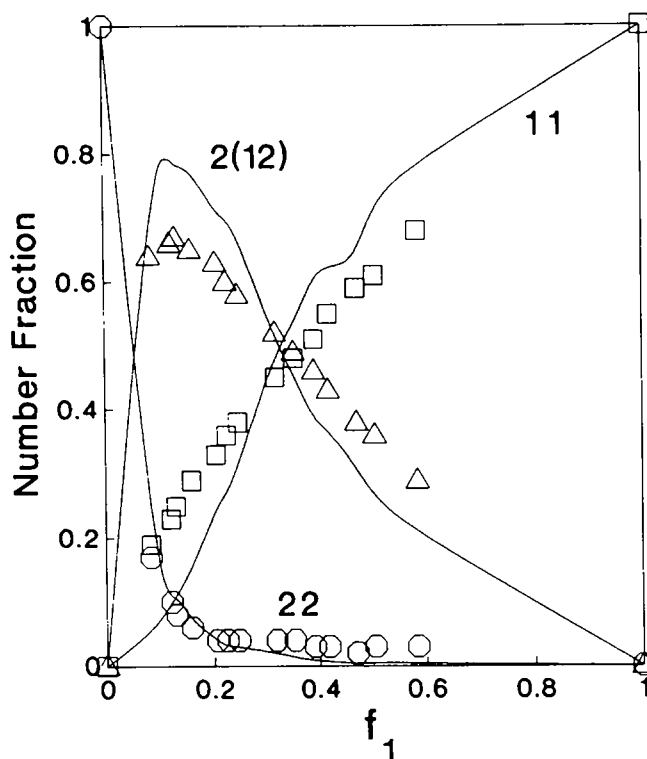


Figure 6 Diad distribution (11, 22 and 12) of VC(1)/IB(2) copolymers as a function of  $f_1$ . Continuous curve is theoretical; symbols are experimental values

three systems encompassing a wide range of conversions. Table 1 is particularly interesting in this respect, since SLD data for the same  $f_1$  and different  $\theta$  are available. It is apparent from this table that, apart from the well established overestimate of like-like fractions for very

**Table 1** Diad distribution of VC(monomer-1)/VA(monomer-2) copolymers. The calculated values have been obtained via the MSM with the following input values:  $r_1 = 6.7$ ;  $r_2 = 0.05$  and  $N = 30000$ . Feed compositions and fractional conversions are given in the table

$f_1$	$\theta$	$P_{11}$	$P_{22}$	$f_{11}$		$f_{12}$		$f_{21}$		$f_{22}$	
				Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0.049	0.15	0.26	0.49	0.03	0.03	0.26	0.22	0.26	0.22	0.45	0.54
0.11	0.066	0.45	0.288	0.22	0.19	0.32	0.35	0.32	0.35	0.14	0.11
0.19	0.049	0.61	0.176	0.38	0.47	0.28	0.25	0.28	0.25	0.05	0.03
0.19	0.61	0.61	0.176	0.11	0.12	0.21	0.19	0.21	0.19	0.48	0.50
0.29	0.043	0.73	0.11	0.55	0.63	0.21	0.18	0.21	0.18	0.04	0.01
0.39	0.038	0.81	0.073	0.67	0.78	0.16	0.11	0.16	0.11	0.01	0.0
0.39	0.08	0.81	0.073	0.66	0.76	0.16	0.12	0.16	0.12	0.03	0.0
0.39	0.14	0.81	0.073	0.63	0.76	0.18	0.12	0.18	0.12	0.01	0.0
0.39	0.53	0.81	0.073	0.45	0.49	0.24	0.22	0.24	0.22	0.06	0.07
0.39	0.71	0.81	0.073	0.35	0.37	0.20	0.18	0.20	0.18	0.25	0.28
0.49	0.036	0.87	0.05	0.75	0.85	0.12	0.08	0.12	0.08	0.0	0.0

**Table 2** Diad distribution of ES(monomer-1)/PS(monomer-2) copolymers. The calculated values have been obtained via the MSM with the following input values:  $r_1 = 2.12$ ;  $r_2 = 0.46$  and  $N = 30000$ . Feed compositions and fractional conversions are given in the table

$f_1$	$\theta$	$P_{11}$	$P_{22}$	$f_{11}$		$f_{12}$		$f_{21}$		$f_{22}$	
				Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0.10	0.40	0.19	0.81	0.02	0.01	0.11	0.10	0.12	0.10	0.75	0.78
0.15	0.13	0.27	0.72	0.08	0.04	0.21	0.16	0.21	0.16	0.50	0.65
0.20	0.71	0.35	0.65	0.07	0.05	0.17	0.18	0.17	0.18	0.60	0.60
0.25	0.19	0.41	0.58	0.15	0.11	0.24	0.23	0.24	0.23	0.38	0.44
0.30	0.90	0.48	0.52	0.12	0.11	0.21	0.21	0.21	0.21	0.47	0.47
0.35	0.98	0.51	0.49	0.16	0.14	0.22	0.21	0.21	0.21	0.41	0.43

**Table 3** Diad distribution of PS(monomer-1)/IBS(monomer-2) copolymers. The calculated values have been obtained via the MSM with the following input values:  $r_1 = 1.44$ ;  $r_2 = 0.64$  and  $N = 30000$ . Feed compositions and fractional conversions are given in the table

$f_1$	$\theta$	$P_{11}$	$P_{22}$	$f_{11}$		$f_{12}$		$f_{21}$		$f_{22}$	
				Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0.35	1	0.44	0.54	0.13	0.12	0.23	0.23	0.23	0.23	0.41	0.42
0.40	1	0.49	0.49	0.17	0.16	0.24	0.24	0.24	0.24	0.35	0.36
0.50	1	0.68	0.30	0.40	0.37	0.24	0.23	0.24	0.23	0.13	0.17

dissimilar ( $P_{11}$ ,  $P_{22}$ ) pairs, this effect diminishes as long as  $\theta$  increases (see for example,  $f_1 = 0.39$  and the different  $\theta$ ). Tables 2 and 3 emphasize and confirm all the observations given before.

To conclude, although not universally applicable, the MSM of the copolymerization of vinyl monomers affords reliable SLD data of both types:  $f_{in}$  as a function of  $n$  and normalized fractions of different diads, triads, tetrads, etc. as a function of  $f_1$  for any  $\theta$  value, in a simple manner, which simplifies enormously the tedious work of structure determination via n.m.r.

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## NOMENCLATURE

$a$	Integer: multiplier
$c$	Integer: increment
$\langle C_c \rangle$	Mean cumulative mole fraction of monomer 1 in stochastic chain
$C_1$ and $C_2$	Molar concentrations in the feed of monomers 1 and 2
$f_1$ and $f_2$	Feed mole fractions of monomers 1 and 2
$f_{in}$	Mole fraction of monomer units of type 1 or 2 within segments of $n$ consecutive units of either monomer 1 or 2. $i$ is either 1 or 2
$F_1$ and $F_2$	Instantaneous copolymer composition
$I_1$ and $I_2$	Relative reactivities of monomers 1 and 2 towards the initiator radical
$K_j, R$	Random number
$n$	Sequence of $n$ units of either monomer 1 or 2
$N$	Initial total number of molecules
$P_{i1}$ and $P_{i2}$	Probabilities of addition of monomer 1 or 2 to the initiator radical
$P_{ij}$	Propagation probabilities
$r_1$ and $r_2$	Reactivity ratios of monomer 1 and 2
$\langle \chi^2 \rangle$	Mean value of the chi-square parameter
$\theta$	Fractional conversion
$\theta_f$	Final conversion