

STUDY ON THE SEQUENCE STRUCTURE OF SBR BY ^{13}C -NMR METHOD VI MONTE CARLO SIMULATION OF THE SEQUENCE OF SBR

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ABSTRACT

A program of Monte Carlo simulation of binary copolymerization for E-SBR (emulsion polymn. SB rubber) was made according to the terminal model. The simulation results obtained by this program were in good agreement with those experimental ones. A detail microstructure information of E-SBR molecular chain has been provided.

INTRODUCTION

In parts I-III of our work^[1-3], the assignments of peaks on ^{13}C -NMR spectra of various SBR samples were made by using "corresponding analysis" method and the calculation formulas which could be used to calculate the microstructure have been deduced.

However, because of overlapping of different degrees of some peaks, the error of the peak intensities represented by peak height and the confinement in the instrument resolving power, up to now there is no method to measure the sequence structure above diad units in SBR chains in using ^{13}C -NMR technique. In order to remedy the defect of ^{13}C -NMR technique in the characterization of SBR and obtain the further information of fine structure, we have simulated the molecular chains of SBR using Monte Carlo method in the present paper. The Monte Carlo method used for the study of polymer molecular chain has been reported by several workers^[4-7], but no paper was concerned in the study of SBR structure. The advantages of Monte Carlo method are that it has much greater flexibility than other statistic simulation and better visualization of the polymer chain, i.e. one can "observe" the sequence structure of a special molecule (Fig.1), which makes it possible to explore the relationship between microstructure and polymer bulk properties, such as the viscoelastic and mechanical properties. A more detailed study of the latter is now in progress in our laboratory.

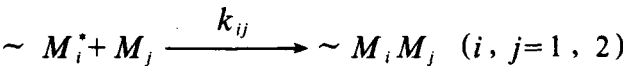
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.....STTCTTSCVSSSTTVTTSTSTTTVTVSTVCVTTTSTTTTVTTVSCC
TSCVTTTTTSSCVVTCCTVSTTVTSTTTSTTTVCCTCCTVTTVTTSSV
TTTSTTTTVTTVSCCTSCVTTTTTSSVCCVVTCTTVSTTVTSTTTSTV
TCTCCTVTTTVTVTSSVCTSTTTCTTSCVSSSTTVTSCCTSTTTVTT.....
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Fig.1 Partially simulated E-SBR molecular chain,
S is Styrene, C, T and V are *cis*, *trans* and vinyl
configurations of butadiene respectively

EXPERIMENTAL

Random numbers are the most important condition for Monte Carlo studies . Here we used the multiplicative congruential method to generate a pseudo-random number sequence on the (0 , 1) interval , so as to ensure the independence and uniformity of the pseudo-random numbers .

The polymerization model is formed by binary copolymerization between styrene (S) and butadiene (B), which has four unit reactions of chain propagation :



here $\sim M_i^*$ is the propagating chain of end unit M_i , M_j is the monomer , and r_{ij} is the reactivity ratios of monomer M_i , which is defined

$r_{ij} = k_{ii} / k_{jj} \quad i, j = 1, 2 \text{ and } i \neq j$

The conditional probability for adding monomer unit M_j to a given chain end unit $\sim M_i^*$, P_{ij} is

$P_{ij} = 1 / (1 + r_{ij} x_i / 1 - x_i)$

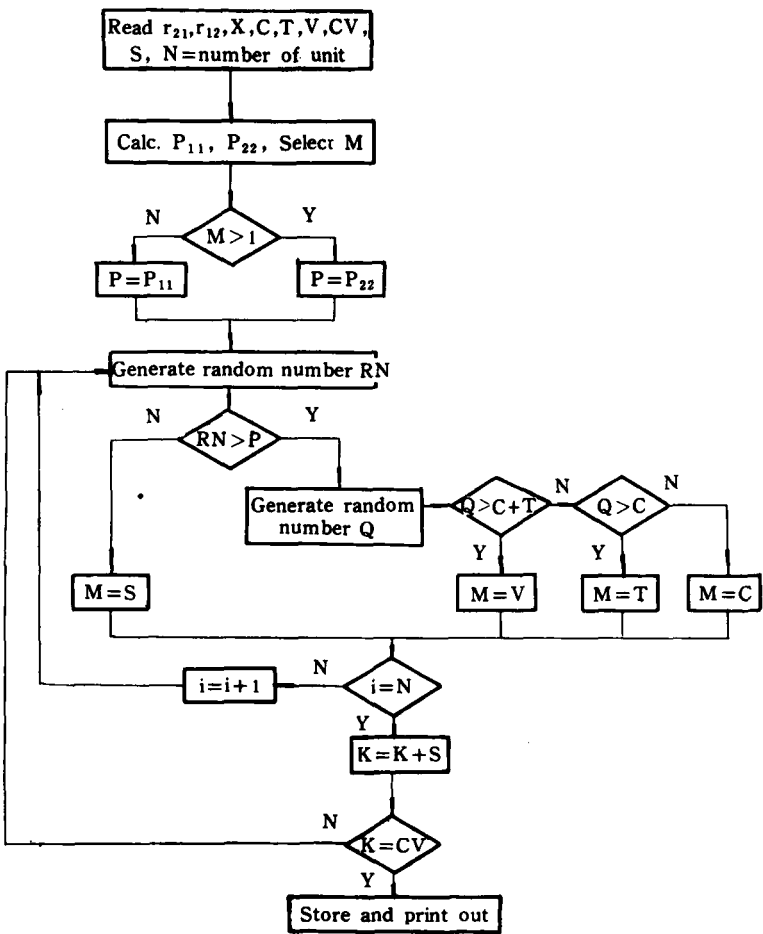


Fig.2 Flow diagram of Monte Carlo simulation for SBR

where x_i is the feed mole fraction of monomer M_i . Because it is a binary system ,

$$P_{ii} + P_{ij} = 1$$

As the present end unit has been fixed , the following reaction step could be determinated using conditional probability p_{11} or p_{22} . When adding a butadiene unit , three probable structures , i.e. C (*cis*) , T (*trans*) and V (vinyl) will exist . Our experiments have demonstrated that the composition of butadiene microstructure is only dependent on the polymerization temperature instead of the conversion in a given polymerization system . So it is possible to use the contents of three microstructures , which can be obtained from the ^{13}C -NMR data , to represent their occurrence probabilities respectively .

In the simulation program , the effect of polymerization conversion on composition distribution has been considered . A flow diagram for the Monte Carlo simulation program of E-SBR is shown in Fig.2 , where CV is the conversion of the sample and S is the conversion increment .

The illustrative rubber sample , we worked with , was obtained from the emulsion polymerization of St and Bd according to the standard E-SBR 1500 recipe : temperature 5.5 $^{\circ}\text{C}$, feed ratios B/S=72/28 (wt.) and conversion 67.4% . Values of reactivity ratios are from the literature , $r_{21}(\text{S})=0.64$, $r_{12}(\text{B})=1.38^{[8]}$. The conversion increment was assumed to be 0.05 . The preparation and structural parameters of E-SBR sample were the same as those of our first report $^{[1]}$.

RESULTS AND DISCUSSION

The simulation results of monomeric unit composition are listed in Table 1 . It could be seen from Table 1 that when simulation numbers of chain length are above 5000 , simulated values are close to , or converge to the results obtained from the experimental ones . Table 2 is the simulating results of diad unit composition of the copolymer . It is obvious that simulated values and the experimental values that could be obtained now are also basically consistent with each other . These facts verify that the chain unit distribution of E-SBR copolymer fits with the assumption of the terminal model , which could imply that the triad and tetrad unit data of the copolymer (see Table 3 and 4) are true and able to provide a further information for the microstructure in E-SBR molecules .

Table 1 Monomeric unit composition distribution of E-SBR

			C	T	V	S
Exp . values			9.30	62.85	14.70	13.01
Sim . values	N=	500	11.40	59.00	16.90	13.00
		1000	9.60	63.20	13.90	13.30
		2000	8.96	64.02	14.70	12.30
		3000	9.20	62.70	15.00	13.20
		5000	9.45	62.25	15.05	12.95
		10000	9.50	62.86	14.64	13.00

Table 2 Diad composition distribution of E-SBR

	CC	TT	CT	TC	CV	VC	CS	SC
EXP .	0.0140	0.3964	0.0530		0.0180		0.0124	
SIM .	0.0120	0.3918	0.0585	0.0680	0.1651	0.1801	0.0130	0.0123
	ST	TS	TV	VT	SS	VV	VS	SV
EXP .	0.0640		0.0987					
SIM .	0.0723	0.0807	0.0930	0.0985	0.0166	0.0215	0.0186	0.0201

Table 3 Triad composition distribution of E-SBR

SSS = 0.0014	SSC = 0.0008	SST = 0.0092	SSV = 0.0022
CSS = 0.0019	CSC = 0.0008	CST = 0.0069	CSV = 0.0021
TSS = 0.0080	TSC = 0.0088	TST = 0.0504	TSV = 0.0124
VSS = 0.0020	VSC = 0.0024	VST = 0.0124	VSV = 0.0030
SCS = 0.0016	SCC = 0.0016	SCT = 0.0091	SCV = 0.0016
CCS = 0.0004	CCC = 0.0008	CCT = 0.0052	CCV = 0.0013
TCS = 0.0081	TCC = 0.0052	TCT = 0.0366	TCV = 0.0101
VCS = 0.0012	VCC = 0.0014	VCT = 0.0086	VCV = 0.0018
STS = 0.0092	STC = 0.0075	STT = 0.0501	STV = 0.0137
CTS = 0.0088	CTC = 0.0050	CTT = 0.0375	CTV = 0.0083
TTS = 0.0520	TTC = 0.0354	TTT = 0.2492	TTV = 0.0585
VTs = 0.0107	VTC = 0.0100	VTT = 0.0610	VTV = 0.0138
SVS = 0.0014	SVC = 0.0018	SVT = 0.0112	SVV = 0.0023
CVS = 0.0028	CVC = 0.0011	CVT = 0.0103	CVV = 0.0013
TVS = 0.0124	TVC = 0.0102	VVT = 0.0590	TVV = 0.0145
VVS = 0.0028	VVC = 0.0017	TVT = 0.0141	VVV = 0.0030

Table 4 Partially tetrad composition distribution of E-SBR

SSSS = 0.0006	CTCV = 0.0017	TTTC = 0.0231
TTSS = 0.0054	TCCV = 0.0010	STST = 0.0066
TVSS = 0.0014	TVCV = 0.0021	TTST = 0.0306
TSCS = 0.0010	TTTV = 0.0062	CTCT = 0.0032
TTCS = 0.0055	TVTV = 0.0069	TTCT = 0.0262
VTCS = 0.0010	SSVV = 0.0011	STTT = 0.0305
SVTS = 0.0015	STVV = 0.0081	TTTT = 0.1625
TSTS = 0.0075	SVVV = 0.0016	TVTT = 0.0369
TTTS = 0.0356	CSVV = 0.0013	VVTT = 0.0091
VSTS = 0.0015	CTVV = 0.0067	TTVT = 0.0391
VTTs = 0.0065	TCVV = 0.0058	TVVT = 0.0096
TCVS = 0.0015	TTVV = 0.0371	VTVT = 0.0083
VTVS = 0.0020	VTVV = 0.0091	VVVT = 0.0011

Keywords :

Monte Carlo simulation ; Styrene-butadiene copolymerization ; Molecular chain microstructure and sequence distribution

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