from electron microscopy *versus* values from neutron scattering. All the EM radii lie below the SANS values, and by about the same amount. Stribeck[15], in a study of lamellar polypropylene utilizing electron microscopy and SAXS, found a similar discrepancy: the lamella thickness he obtained from the EM photos gave values around 30% smaller than those from SAXS analyses. In this case, the samples were stained with chlorosulphonic acid. Inoue *et al.*[16] have noted that the staining procedures they used affected only the outer shell of the microdomains. It seems likely that this is a general characteristic of staining procedures, and one that might be addressed in more detail as a possible source of the discrepancy reported here.

ACKNOWLEDGEMENTS

This research was supported by the National Science Foundation, Division of Materials Research–Polymers Program under grant DMR-8001674 with additional help from DMR-7824185. SANS experiments were performed at the National Center for Small-Angle Scattering Research (NCSASR) which is funded by NSF grant DMR-7724458 through interagency agreement 40637-77 with DOE. The Center is operated by Union Carbide Corporation under DOE contract W-7405-eng-26. The assistance of Dr George Wignall of NCSASR is gratefully acknowledged, and we thank Dr George Hadziioannou of the University of Massachusetts, Amherst, for obtaining the SAXS data. We have also benefitted from the availability of plotting routines developed by Chris Schwier and Martin Suenson, and from stimulating conversations with Dale Handlin and Professor E. L. Thomas of the University of Masschusetts, Amherst.

REFERENCES

1 Roche, E. J. and Thomas, E. L. *Polymer* 1981, **22**, 333
2 Guinier, A. and Fournet, G. 'Small-Angle Scattering of X-Rays', Wiley, New York, 1955
3 Jacrot, B. *Rep. Prog. Phys.* 1976, **39**, 911
4 Bates, F. S., Cohen, R. E. and Berney, C. V. *Macromolecules* 1982, **15**, 589
5 Bates, F. S. *Sc.D. Thesis*, Department of Chemical Engineering, MIT, January 1982
6 Bates, F. S., Berney, C. V. and Cohen, R. E. to be published
7 Bates, F. S. and Cohen, R. E. *Macromolecules* 1981, **14**, 881
8 Kato, K. *Polym. Lett.* 1966, **4**, 35
9 Bacon, G. E. 'Neutron Diffraction', Oxford, London, 1962
10 Hosemann, R. and Bagchi, S. N. 'Direct Analysis of Matter by Diffraction', North Holland, Amsterdam, 1962
11 Hashimoto, T., Fujimura, M. and Kawai, H. *Macromolecules* 1980, **13**, 1660
12 Koberstein, J. T., Morra, B. and Stein, R. S. *J. Appl. Crystallogr.* 1980, **13**, 34
13 Richards, R. W. and Thomason, J. L. *Polymer* 1981, **22**, 581
14 Warren, B. E. *J. Appl. Crystallogr.* 1978, **11**, 695
15 Stribeck, N. *Ph.D. dissertation*, Philipps-Universität, Marburg/Lahn, 1980
16 Inoue, T., Soen, T., Hashimota, T. and Kawai, H. *Macromolecules* 1970, **3**, 87

Monte Carlo simulation of radiation-induced solid state polymerization

Piotr Romiszowski and Andrzej Kolinski
Department of Chemistry, University of Warsaw, 02-093 *Warsaw, Poland*
(*Received* 13 *July* 1981*; revised* 19 *February* 1982)

A Monte Carlo method was used for a computer simulation of radiation-induced solid state polymerization. The propagation of polymer chains was simulated by means of self-avoiding random walks on a tetrahedral lattice. The initiation and termination of the chains were modelled by pseudo-random processes. The influence of conditions of the in-source process on the post-polymerization kinetics and on the degree of polymerization of the polymers was studied.

Keywords Polymerization; Monte Carlo simulation; radiation-induced polymerization; post-effect; kinetics; random walk

INTRODUCTION

This report is a continuation of former papers on the computer simulation of solid state polymerization processes using Monte Carlo methods. The first paper[1] considered a model of post-polymerization neglecting chain growth during the irradiation. In the second[2], a radiation-induced in-source solid state polymerization model was presented. Both these models were idealized descriptions of real, two-stage polymerization processes.

It is the intention of this report to combine the two aforementioned models and examine the results obtained.

When considering the process of solid state polymerization initiated by irradiation, two basic stages can be distinguished:

(1) Formation of new active centres in the irradiated monomer sample and the simultaneous growth of polymeric chains.

(2) Further growth of the chains after removing the sample from the source of radiation (post-polymerization).

In both stages, the termination of chain growth occurs by the trapping of the macroradicals in the mass of the polymer. Such a formulation of the problem is the basis of the pseudostochastic model.

DESCRIPTION OF THE SIMULATIONS

The algorithm constructed is based on the Monte Carlo technique of generating random walks on spatial lattices[3,4]. A tetrahedral lattice was used in the computations. The basic assumptions of the model are the

0032-3861/82/081226–04$03.00

following:

(1) The solid state sample of monomer is represented by a chosen lattice in the form of cuboid. It is assumed that each of the lattice points contains one molecule of monomer. The presence of lattice defects and diffusion phenomenons are ignored in these computations.

(2) The generating process of active centres resulting from irradiation has been simulated by the random choice of coordinates of the lattice points. It is assumed that the probability of the appearance of an active centre in every site of the lattice is identical.

(3) Non-intersecting random walks on the lattice are treated as growing polymer chains. All chains grow in the aforementioned cubic box and periodic boundary conditions are employed[5].

(4) All chains are simultaneously generated by adding successive segments. If the addition of a new segment to any of the growing chains leads to double occupancy of the lattice point, then the segment is not added. The attempt to add a new segment is made during the next cycle of the program. Thus the decrease of the monomer concentration makes the chain growth slower. In the case of the complete polymerization of the monomer, in the vicinity of the end of growing macroradical, the chain growth stops. The number of lattice points occupied by one random walk is treated as the degree of polymerization of the model macromolecule.

(5) To enable an examination of the kinetics of the model process to be made, a time parameter was introduced into the algorithm. It was assumed that unit time is that required to perform a single attempt at adding one segment to a chain. In all computations it is assumed that the propagation rate constant is $K_p = 1$. Therefore the probability of addition of a new segment to the growing chain in unit time is exactly equal to the local fraction of lattice points occupied by monomer molecules.

The values of radiation dose power (I) varied from 0.2 to 1.0 with an increment 0.2. It is evident that I is an equivalent of the rate constant of the initiation process. $I = 1.0$ the case where the formation of one new active centre takes place in unit time.

(6) The ratio of the number of lattice points occupied by all model chains to the total number of lattice points is understood as the degree of conversion (S).

(7) The end of the polymerization and the beginning of the second stage of the process (post-polymerization) occurs when the conversion reaches a certain *a priori* assumed value S_1. During the whole computation the conversion of monomer into polymer and the degree of polymerization were traced and the final results gave the polymer mass distribution.

RESULTS AND DISCUSSION

Computations were made for various sets of input data I and S_1. *Figures 1–3* show the kinetic dependence of conversion *versus* time. The curves are drawn so that the beginning of the post-polymerization is situated on the same point of the t-axis. It is noticeable that these curves are S-shaped, reaching a certain plateau which is the maximum conversion S_{max}. Curves of this shape have been observed in the case of a solid state polymerization[1]. In the first stage of the process one can observe the increase in the rate of polymerization, caused by the formation of new active centres. The rapid decrease in the amount of monomer in the second stage of the process and the trapping of the growing macroradicals in the polymer mass cause a reduction in the rate of polymerization until termination. The influence of steric interactions on the chain growth were observed empirically[6] as well as theoretically predicted in analytical models as a so-called 'umbrella effect'[7].

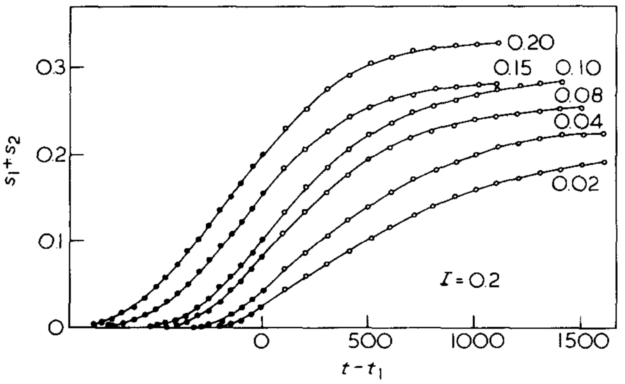


Figure 1 Monomer to polymer conversion $S = S_1 + S_2$ vs. time for $I = 0.2$ and different values of in-source conversions indicated. Curves are drawn so that the time of post-polymerization $(t - t_1)$ is counted from the same point on t-axis for each curve

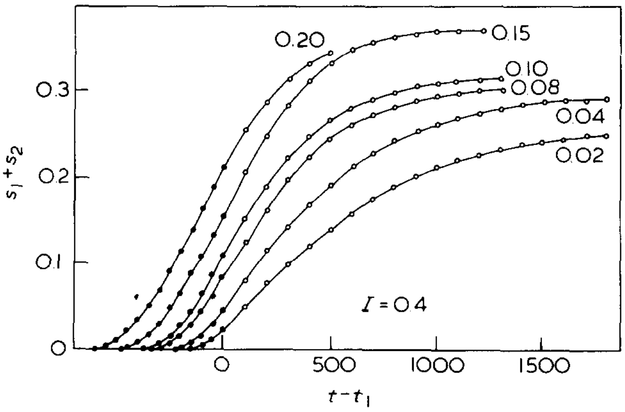


Figure 2 Plots of conversion vs. time for $I = 0.4$

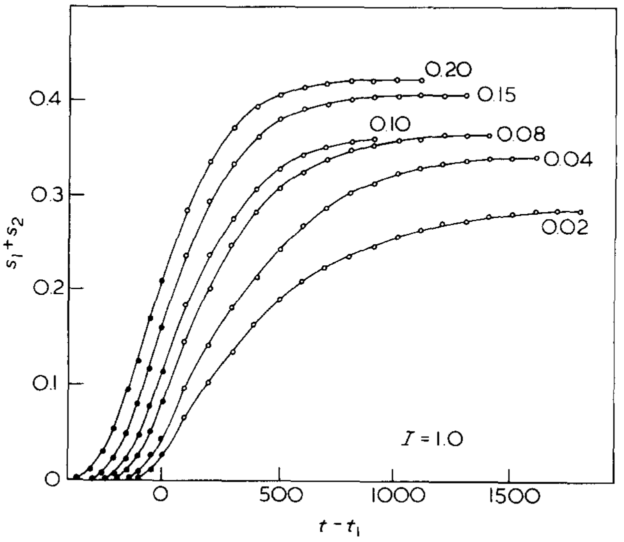


Figure 3 Plots of conversion vs. time for $I = 1.0$

Comparing the set of kinetic curves one can notice that the increase in in-source degree of conversion leads to a higher final conversion, which corresponds to the flat areas on these curves. Also an increase in the rate of post-polymerization for higher values for the in-source conversion is observed (*Figure 4*). This phenomenon had been described in empirical studies of solid state polymerization[8]. It can easily be explained by the fact that the rate of post-polymerization is wholly connected with the number of active centres formed during the irradiation. The increase in the rate of post-polymerization with the increase in radiation dose can be interpreted in the same way (see *Figure 4*).

The described Monte Carlo model enables us to analyse the influence of the kinetics of the process on the properties of the final polymer. The histograms of the distribution of the degree of polymerization for different values of in-source conversions (S_1) and a constant value of the radiation dose $I = 0.4$ are shown in *Figure 5*. One can observe the decrease in the polymer polydispersion for a longer period of in-source irradiation. Also the average degree of polymerization (*DP*) decreases with the increasing time of the irradiation as well as with the increase in radiation dose, which is shown in *Figure 6*.

The model contains several simplifications requiring further discussion. The basic simplification is that the polymer molecules as well as the monomer can be represented by means of the same spatial lattice. Also the crystal defects of the lattice are ignored. It may cause some errors which may decrease the resulting conversion particularly in high conversions.

Also the discounting of monomer diffusion may cause a decrease in the polymerization rate, in particular with very slow polymerization processes.

The mechanism of chain termination, as a result of complete polymerization of the monomer in the vicinity of the active macroradical, is a consequence of the fixing of the position of monomer molecules and polymer chains in the lattice. Thus the simplifications of the model may lead to prediction of slightly lower values of high post-effect conversions.

However, the simplicity of the model assumptions allows explicit determination of the influence of basic parameters on the process, its kinetics and the mass distribution of the polymer. The results may create the basis for future analysis of the special effects.

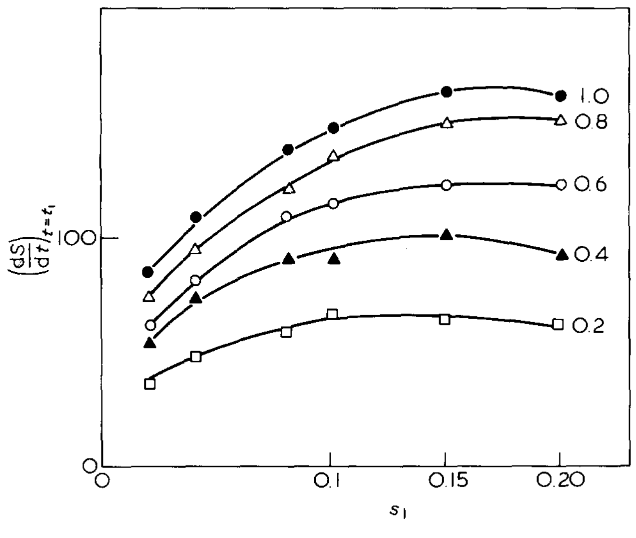


Figure 4 The initial rate of post-polymerizations vs. in-source conversion S_1 for different values of radiation dose *I* indicated

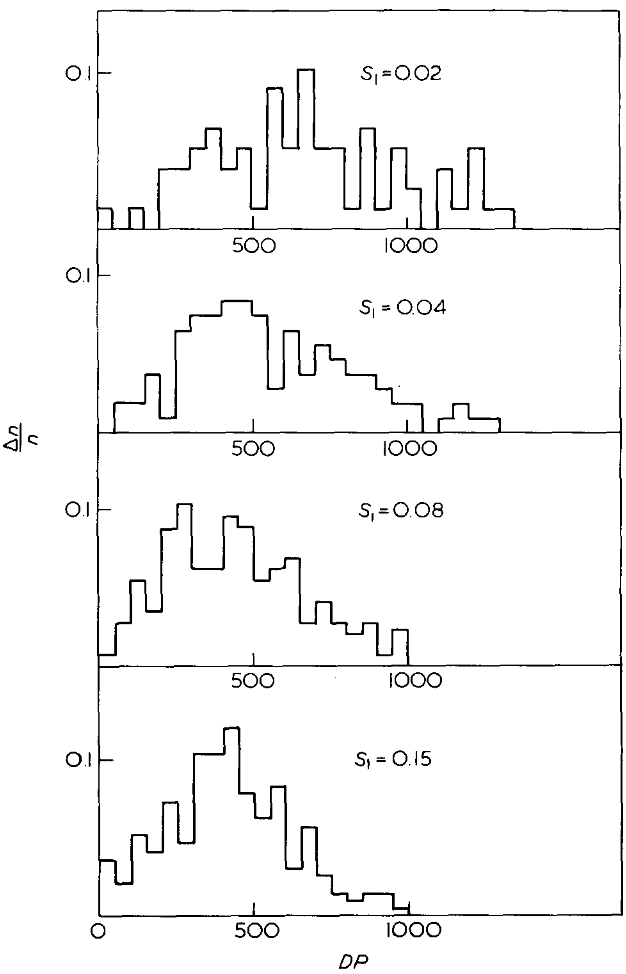


Figure 5 Degree of polymerization distributions for *I* = 0.4 and different values of in-source conversions

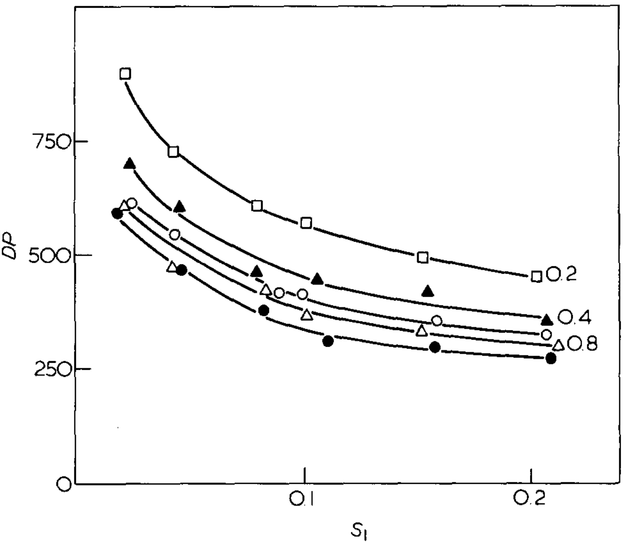


Figure 6 Plots of the final average degree of polymerization vs. in-source conversion for different values of *I* indicated

CONCLUSIONS

The stochastic model of the solid state polymerization presented here is based on several simple assumptions and in spite of their simplicity the process is described quite satisfactorily. The two facts which should be emphasized are (1) that the results of the computation experiments are the consequence of the precisely defined mechanism of the process, without any additional assumptions being made, which are necessary in the formal kinetics. (2) That the proposed model enables us to achieve a fuller description of the polymerization. It is possible to watch the course of micro- and macroprocesses and to obtain consistent information even for those processes which are difficult to achieve by direct experimentation.

Both the above mentioned attributes of the computational model described here permit us to use it as a semi-empirical method to predict the results of real polymerization processes.

REFERENCES

1 Orszagh, A. and Romiszowski, P. Proc. of the Fourth Tihany Symposium on Radiation Chemistry, Akademiai Kiado, Budapest 1977, p. 387

2 Orszagh, A., Koliński, A. and Romiszowski, P. *Polymer* 1979, **20**, 113

3 Jurs, P. C. and Reissner, J. E. *J. Chem. Phys.* 1971, **55**, 4948

4 Jurs, P. C. and Reissner, J. E. *J. Chem. Phys.* 1973, **58**, 5309

5 Metropolis, N., Rosenbluth, A. W., Rosenbluth, M. N., Teller, A. H. and Teller, E. *J. Chem. Phys.* 1953, **21**, 1087

6 Chachaty, C. and Forchioni, A. *J. Polym. Sci. A-1* 1972, **10**, 1905

7 Boucher, E. A. *J. Chem. Phys.* 1973, **59**, 3848

8 Bensasson, R. and Bernas, A. *J. Polym. Sci.* 1958, **30**, 163

The acid catalysed condensation of phenol-4-sulphonic acid with formaldehyde

J. Guthrie and I. I. Sada
Department of Industrial Chemistry, The Queen's University of Belfast, Belfast BT9 5DL, UK
(*Received* 26 *January* 1982)

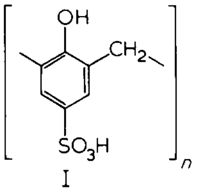
The reaction products formed when phenol-4-sulphonic acid reacts with formaldehyde have been investigated using ^1H and ^{13}C nuclear magnetic resonance. It is shown that the reaction does not proceed readily at high phenol-4-sulphonic acid: formaldehyde ratios. As the ratio is decreased evidence of reaction is observed and further decreases lead to crosslinking. The crosslinking reaction is explained in terms of desulphonation and electrophilic substitution of the sulphonic acid group by a hydroxymethylene carbonium ion.

Keywords Phenolsulphonic acid; formaldehyde; condensation reaction; acid catalysis; nuclear magnetic resonance

INTRODUCTION

The resinous reaction products of phenol sulphonic acids with formaldehyde are well known, particularly in the formation of synthetic tanning agents[1] for use in the leather industry and also in the formation of cation exchangers[2]. In general synthetic tanning agents are water soluble materials whilst ion exchange resins are of course insoluble.

Many papers and patents have reported the polycondensation of sulphonated phenol with formaldehyde. These investigations have been mainly concerned with the manufacture and final properties of the products which may give them commercial importance. However, very little work has been carried out on the chemistry of the condensation reaction of phenol sulphonic acid and formaldehyde under acid catalysed conditions. The many references to patents[3] claim that the polycondensation will yield a sulphonated polymer which depending on the reaction conditions may be either soluble or insoluble in water. Since the sulphonation of phenol gives predominantly *p*-phenol sulphonic acid it would be normally expected that the resulting product could be represented as (I), i.e. a sulphonated novolak. However, as it is well known that insoluble materials can be formed under appropriate conditions it was decided to investigate the reaction between *p*-phenol sulphonic acid and formaldehyde in dilute solution under acid conditions.



I

EXPERIMENTAL

Materials

All of the phenolic compounds used in this work were of analytical reagent grade purchased from Aldrich Chemical Co. Inc. Formaldehyde was used in the form of an aqueous solution 39–41% w/v.

Synthesis of phenol-4-sulphonic acid[4]

Phenol (53 g) was sulphonated with concentrated sulphuric acid (98%) at 120°C as described by Coffey. Yield 82.75 g. The ^{13}C spectra (*Figure 1*) shows the existence of only four different carbon atoms as would be expected in the symmetrical *p*-isomer.

Reaction between phenol-4-sulphonic acid and formaldehyde

The appropriate weight of phenol sulphonic acid was

0032–3861/82/081229–04$03.00