Network structure in epoxies: 6. The growth process investigated by neutron scattering

Wen-li Wu and Barry J. Bauer
Polymers Division, Institute of Material Science and Engineering, National Bureau of Standards, Gaithersburg, MD 20899, USA

and Weijie Su
The Shanghai Institute of Pharma and Technology, Shanghai, China

(Received 29 September 1988; accepted 21 October 1988)

The curing process of epoxies in bulk prior to the gelation threshold was investigated using small-angle neutron scattering. Both the radius of gyration and the molecular weight of the partially cured molecular networks were measured at various extents of cure. Two curing agents with different functionality were used to elucidate the curing mechanism. The experimental results were interpreted in terms of the classical Flory–Stockmayer theory and the percolation theory.

(Keywords: network; epoxies; neutron scattering; Flory–Stockmayer theory; percolation theory)

INTRODUCTION

The gelation of long-chain polymers in bulk and in solution has been the subject of many theoretical[1–7] and experimental studies[8–10]. For long-chain molecules in the melt or in semidilute solution, the crosslinking or gelation can be modelled through the classical Flory–Stockmayer (FS) theory[1,2,6]. In solution below the overlap concentration, the gelation of long-chain molecules follows the critical behaviour of percolation theory[11,12]. Such a critical behaviour was also observed in the gelation of entities without interpenetration. One of many good examples of this case is the aggregation of silica particles[13]. In such a system the excluded volume of the particles is not screened, contrary to what happens to long-chain polymers in bulk or in concentrated solutions. It is the excluded-volume effect of the building blocks in the reaction environment that dictates the gelation process to be either the FS type or the critical type[6,14].

In the crosslinking of epoxies, the size (molecular weight) of the building block (monomer) is typically in the range of 10^2 to 10^3 g mol^{-1}. The current trend in the formulation of epoxies for improvement of toughness is to increase the molecular weight of the monomers. The size of epoxy monomers is too small to be considered a long chain, and too large to be considered small particles without any interpenetration in the bulk state. It is therefore of interest to determine if the gelation process of epoxies follows the critical or the classical FS behaviours.

Experiments to investigate the conformation of partially cured epoxies have been conducted[15,16]. The monomers were reacted in the melt, and then dissolved in solvents. Scattering measurements were then conducted to determine the molecular weight, radius of gyration and in one case the fractal behaviour[16]. In the work by Bantle *et al.*[15] a significant amount of difunctional monomer was included in the starting materials. Consequently, the reaction gave rise to some branched molecules and loosely crosslinked networks instead of the tightly crosslinked ones typical of epoxies. For loosely crosslinked networks, theoretical results[17] suggested that the critical region is rather narrow. This could account for the observations of FS-type behaviour in the work of Bantle *et al.* Recent work of Chu *et al.*[16] was concerned with the fractal behaviour in X-ray scattering, and the mass fractal dimension obtained was higher than those of Bantle and those reported in this paper. However, the q range in their experiment was too narrow to determine the fractal dimension directly from the relationship of scattering intensity *versus* q, q being the magnitude of scattering vector defined as $4\pi/\lambda \sin\theta$.

The molecular weight and the radius of gyration are determined through a conventional Zimm plot for a more precise measurement of the fractal dimension of the molecular network. Furthermore, the epoxy system employed in this work is cured via an epoxide–amine addition polymerization. Conceptually this type of polymerization can be modelled with a cluster–cluster aggregation process, which is a widely studied percolation process.

The epoxy monomer is a diepoxide, and in an epoxide–amine type reaction the reaction rate of the secondary amino is slower than that of the primary amino due to a steric effect[18]. The strength of this effect depends on the local structure of the reacting groups. This complicates the interpretation of the experimental data. With a linear diamine as the curing agent, the formation of linear chains is facilitated when the degree of cure is less than 50%. If a tri- or higher-functionality amine is used, a highly branched or crosslinked structure will result even if the reaction of the secondary amine is retarded. Consequently, the experiments were carried out with both diamine and triamine monomers.

0032-3861/89/081384–05$03.00

EXPERIMENTAL

Materials

Diglycyl ether of bisphenol A (DGEBA) was chosen as the epoxy monomer. DER332* (Dow Chemical Co.) was dissolved in a mixed solvent of 40 wt% methyl isobutyl ketone and 60 wt% methyl isobutyl carbanol at room temperature. Recrystallization of the monomer was induced by lowering the mixture to 0°C. The epoxide equivalent molecular weight as determined by titration was 175 for the purified monomer. The diamine and the triamine used were D-230 and T-403 Jeffamines* (Texaco Chemical Co.) respectively. Both of these amines have a narrow molecular-weight distribution, the polydispersities as measured by g.p.c. being $M_w/M_n = 1.08$ and 1.06 for D-230 and T-403 respectively. All of the amine–epoxy mixtures of this study were made with a stoichiometric amount of amino hydrogens and epoxy groups.

Curing procedure

The amine–epoxy mixtures were mixed at room temperature and poured into a sample cell of a Contraves Rheoanalyzer* maintained at 60°C. The cylindrical sample cell was used (0.6 inch diameter, 2 inch length). A rotor is immersed in the sample through which the viscosity is measured. Typical sample size is about 10 g. A shear rate of $30\,s^{-1}$ was maintained throughout the experiment and the viscosity was recorded as a measure of the extent of cure.

To obtain samples close to the fractional conversion at gelation (p_c), the curing temperature was lowered to 21°C from the initial 60°C curing temperature after the shear viscosity reached 50 000 cps. Had the temperature stayed at 60°C, gelation would have been reached within 5 min, and removing samples for scattering measuring within such a short time period would be too difficult. With the temperature lowered to 21°C it took approximately 4 h to reach the gelation threshold, at which time an insoluble solid was formed.

Degree of cure

A portion of each sample was removed from the Contraves Rheoanalyzer for the scattering measurement and was characterized with infra-red (i.r.) to determine the degree of cure (p). In an i.r. measurement, the magnitude of the epoxide absorption band at $920\,cm^{-1}$ wavenumber was measured and the value of p was calculated by comparing that of the uncured starting materials. The precision of the i.r. measurements was less than a few per cent. Consequently, these i.r. data are not reliable enough for the determination of critical exponent relating molecular weight with the degree of undercure (ε) defined as $\varepsilon \equiv p_c - p$.

Scattering measurements

The small-angle neutron scattering (SANS) instrument at the NBS reactor was used for all the measurements. A wavelength of 5 Å was chosen and the q range covered was from 0.007 to $0.2\,Å^{-1}$. Samples removed from the Rheoanalyzer at different stages were dissolved in deuterated tetrahydrofuran (THF) to prepare solutions for the scattering measurements. The concentration of the solutions ranges from 2×10^{-3} to 1×10^{-2} volume fraction. The solutions were kept at 0°C throughout the whole post-cure period, including the scattering measurements. No evidence of further reaction was noticed for samples in solution; some SANS measurements were conducted on the same specimen at the beginning and the end of the test period of about a week, and the results were identical within the experimental uncertainties. For each sample SANS measurements at three or four different concentrations were conducted and the results were analyzed with a Zimm plot. Prior to the Zimm analyses, the scattering intensity was corrected for empty cell, background and incoherent contributions. It was then normalized to a polymer content of unity and reduced to the absolute scale by using a silica-gel sample as a calibration standard.

RESULTS

Infra-red results for DGEBA/D-230 cured at 60°C and subsequently quenched to 21°C are given in *Figure 1*. The precision of the measurements prevents the use of these values of p in a direct computation of critical exponents such as γ, which relates the weight-average degree of polymerization (N_w) to the degree of undercure through the equation $N_w \propto \varepsilon^{-\gamma}$. Hence, *Figure 1* serves only to identify the location of the SANS samples on the curing curve. The absorption at $920\,cm^{-1}$ is not a single band, but is composed of at least one other absorption, which is the major source of error in the i.r. measurement. The second source of error is due to the elapsed time between the i.r. measurement and the removal of material from the Rheoanalyzer. As is demonstrated in *Figure 1*, the cure does proceed at room temperature and the amount of additional cure during the elapsed time is expected to depend on the extent of cure of the samples. For the same amount of elapsed time the material removed from the Rheoanalyzer in the early stage of cure will have larger increment in p than those with high extent

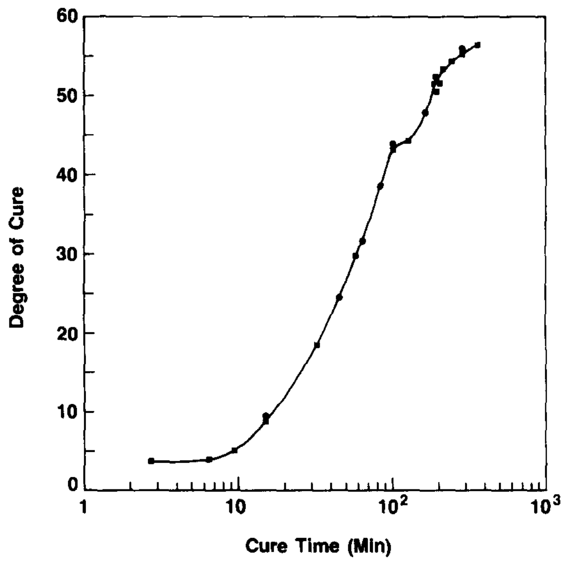

Figure 1 The degree of cure (p) measured with infra-red of DGEBA and D-230 diamine mixture. The cure temperature was 60°C in the first 100 min then lowered to 23°C. The full circles denote where the specimens for small-angle neutron scattering measurement were collected

---

* Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply necessarily the best available for the purpose

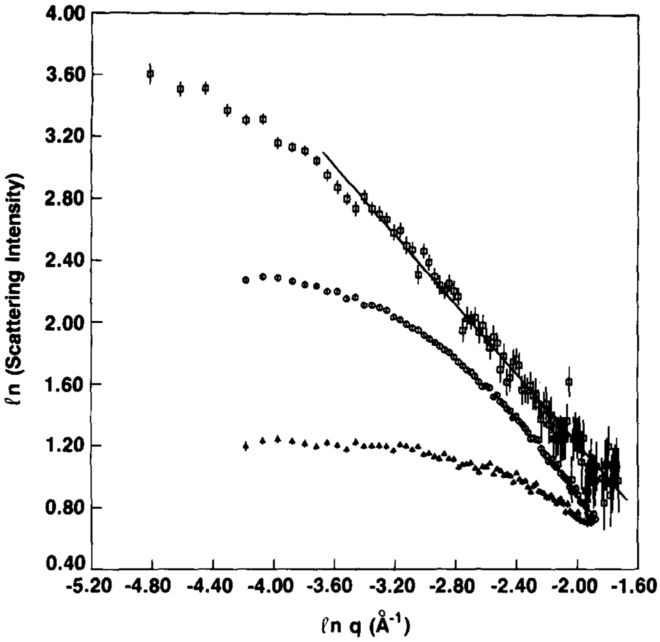

Figure 2 Small-angle neutron scattering results of partially cured DGEBA/D-230 dissolved in deuterated THF. The polymer content is 1.5 vol% for all three measurements with the following values of p: (□) 0.55; (○) 0.36; (▲) 0.25

of cure. Accordingly, the value of p measured does not equal that of the corresponding SANS sample; the i.r. values are believed to be greater than that of the SANS sample. The approximate locations of the SANS samples are denoted by full circles on *Figure 1* in addition to all the other i.r. results denoted by full squares.

SANS results of DGEBA cured with D-230 diamine are given in *Figure 2*. The polymer concentration of the sample was about 1.5 vol%, and the degree of cure is different in the three curves. The values of p determined by i.r. are 0.25, 0.36 and 0.55 for the three curves. The SANS results are presented in a log–log plot. The scattering intensity increases in the low-q region as the degree of cure is increased. Over a limited range of q space a linear behaviour is observed on the sample with the highest degree of cure. The q domain exhibiting the linear scattering behaviour is from 0.02 to 0.2 Å^{-1}, as shown in *Figure 2*. The slope of this linear region is about 1.2. This value of slope is much lower than that observed by Chu *et al.*[16], who report a value of about 2.0.

The slope of log(scattering intensity) *versus* log(q) does not change significantly with the polymer concentration, as is illustrated in *Figure 3*, where SANS results of the sample with $p = 0.48$ at two different polymer contents are given. The most noticeable effect of lowering the polymer concentration is the expansion of the linear region into the low-q domain. This can be explained by the interparticle contribution to the scattering intensity. The lower the polymer concentration, the less the interparticle interference. In a good solvent, such as THF, the interparticle contribution is always negative.

The q region exhibiting a linear or fractal behaviour is limited compared to what was reported by others, e.g. a linear behaviour up to three orders of magnitude was reported by Schaefer and Keefer in silica gel[8]. To improve the precision of the measurement of the mass fractal dimension, both the molecular weight and the radius of gyration of eight samples were determined. The values of p are up to 0.55 for these eight samples. Material with $p > 0.55$ could not be completely dissolved in THF.

Three or four solutions of different polymer concentration were prepared from each of the eight samples. The SANS data were analysed by Zimm plots to determine the values of molecular weight and radius of gyration. The results are given in *Figure 4*. The data points can be fitted with a simple power law: $N_w \propto R_Z^D$ with $D = 1.15$ and where R_Z is the Z-averaged radius of gyration. The abscissa of *Figure 4* is the zero-angle scattering intensity at zero polymer concentration obtained through a Zimm plot. Its value is directly proportional to the molecular weight and the proportionality constant stays the same in all cases. For the determination of the critical exponent D, this proportionality constant can be ignored.

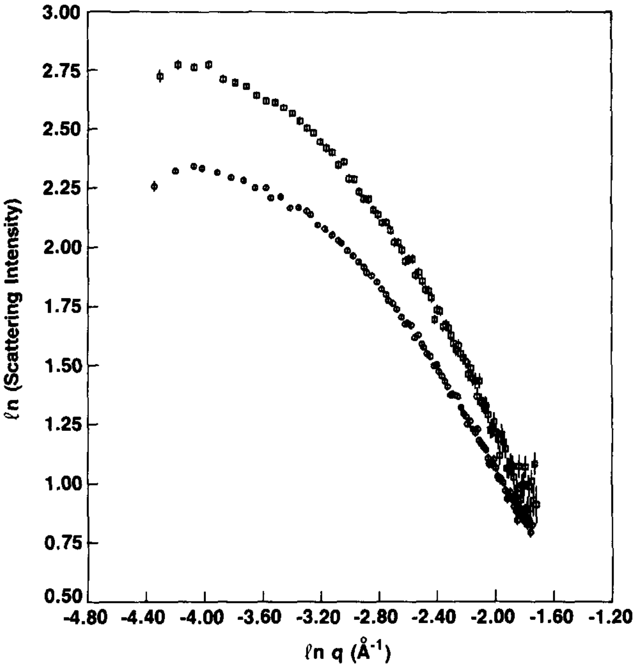

Figure 3 Small-angle neutron scattering results of partially cured DGEBA and D-230 diamine mixture dissolved in deuterated THF. For both curves the degree of cure is 0.48. The polymer content by volume is: (□) 0.7%; (○) 3%

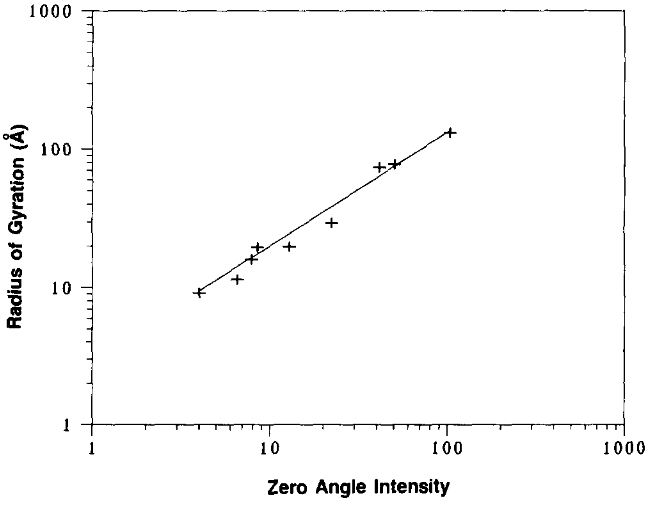

Figure 4 Relationship between the zero-angle scattering intensity and the Z-average radius of gyration measured in partially cured DGEBA and D-230 diamine. Both quantities were obtained through a Zimm analysis of the SANS data

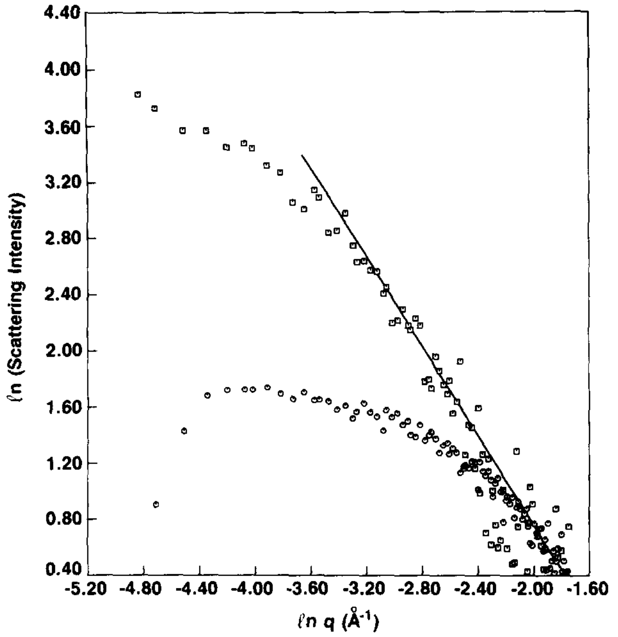

Figure 5 Small-angle neutron scattering results of DGEBA cured with T-403 triamine dissolved in deuterated THF. For both curves the polymer content by volume is 1.5% and the degree of cure is: (□) 3.5; (○) 0.09

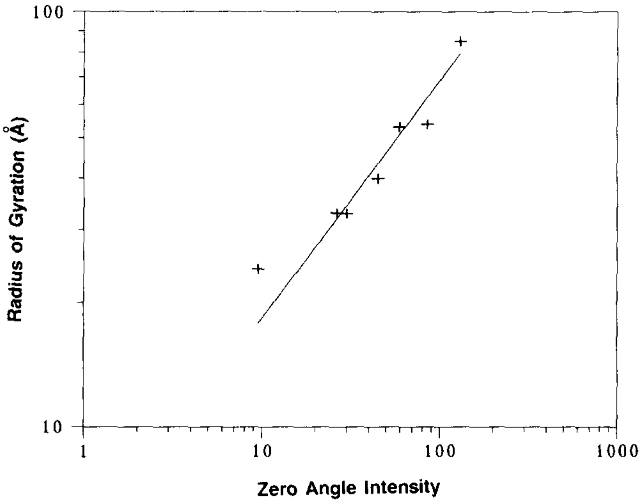

Figure 6 Relationship between the zero-angle scattering intensity and the Z-average radius of gyration measured in partially cured DGEBA and T-403 triamine. Both quantities were obtained through a Zimm analysis of the SANS data

A typical set of SANS results of DGEBA cured with T-403 triamine is given in *Figure 5*; the polymer content for these two curves is about 1.5%. The values of p determined by i.r. are 0.08 and 0.35 for these curves. The sample with a high value of p exhibits linear behaviour in the log(scattering intensity) vs. log(q) plot. The q domain of the linear behaviour is from 0.02 to 0.2 Å^{-1}, which is the same as the D-230 cured samples. However, the slope for this case is 1.6 instead of 1.2 of the D-230 materials.

The same preparation of solutions of different concentrations was used in SANS experiments for each of the eight T-403 samples of different conversions. The range of p measured by i.r. in this study is from 8 to 38%. Samples with $p > 0.4$ could not be completely dissolved in THF. The values of zero-angle scattering intensity and radius of gyration (R_Z) for each of the T-403 cured samples were obtained through Zimm plots. The result is given in *Figure 6* in a log–log plot. Once again, a linear relationship of $N_w \propto R_Z^D$ was observed with $D = 1.67$.

DISCUSSION

The value of D, the apparent mass fractal dimension, observed in the D-230 cured samples is 1.15 through the M_w vs. R_Z relationship, and is 1.2 from the scattering intensity curve from samples with high value of p. The values are 1.67 and 1.6, respectively, by these two methods for the T-403 cured samples.

Within individual gel particles dissolved in a good solvent, the value of D is 2.0 according to the FS theory once the excluded-volume effect is taken into consideration. For gel particles without the excluded-volume effect, the mass fractal dimension is 4.0 for large clusters in the FS theory[19]. According to percolation theory, the value of D is also 2.0 for individual gel particles and 2.5 for a percolated particle at gelation threshold, i.e. $p = p_c$. These values are derived for the presence of an excluded-volume effect, and should prevail in dilute solution measurements using good solvents. However, these theoretical values from either FS or percolation theory are higher than those observed.

In all the SANS measurements of this work, materials were not fractionated to obtain samples of narrower molecular-weight distribution. Consequently, the polydispersity in particle size needs to be included in the interpretation of the observed values of D. This polydispersity in size distribution is present in both FS and the percolation theories, the functional form of the distribution being the same for both theories. The only difference is the values of the critical exponents. According to the work by Daoud *et al.*[20] a simple power law $N_w \propto R_Z^D$ still holds even if the effect of polydispersity is included in each theory. However, the exponent D is no longer the mass fractal dimension of the individual particle or cluster. Instead, the parameter D is a compounded one embracing the fractal dimensions of individual clusters and the exponents specifying the size distribution. Its value is 1.59 for the percolation model and 1.0 for the classical FS theory. The work of Martin and Ackerson[21] further demonstrated that the same exponent would also appear on the scattering behaviour of $I(q) \propto q^{-D}$ after the polydispersity effect was taken into account.

By comparing the observed and theoretical values of D, the D-230 cured samples seem to follow a classical FS behaviour whereas the T-403 ones follow the percolation prediction. It is not a total surprise to observe a percolation behaviour for epoxies cured in bulk if the curing reaction is a polyaddition type. For other types of curing mechanisms, e.g. the anionic mechanism used by Chu *et al.*[16], a diffusion controlling or kinetic gelation model[22,23] might be more appropriate. In a kinetic gelation process, the growth and annihilation of the reactive groups or radicals and other kinetic aspects of the gelation process are considered explicitly. The critical exponents have been found to be different from those of the standard percolation process.

The fact that the T-403 cured samples follow a percolation prediction in terms of the value of D has the following implication. The excluded-volume effect is important among the branches within a gel particle during the reaction, especially for those large clusters which dominate the curing process. These clusters of low molecular weight, including monomers, are regarded as solvent for the large clusters and give rise to the excluded-volume effect. For the D-230 cured epoxy, the mass fractal dimension determined from both the R_Z *versus* M_w relationship and the slope of individual scattering curves is close to that predicted by FS theory. This can be explained by the substitution effect of the amino group. Once the primary amino is reacted with an epoxide, the reaction of the secondary amino is retarded. For diamines, such a substitution effect will result in the formation of linear chains laden with unreacted secondary amino groups. As has been conclusively demonstrated by others[15,20], the gelation of linear chains in bulk follows the FS prediction. The critical region for the gelation of linear chains of reasonably high molecular weight is very narrow[20]. One has to get to a very small ε value to observe the critical behaviour. Presumably our measurements of M_w and R_Z were made outside the critical region.

The q range over which the scattering intensity exhibits a fractal behaviour merits some discussion. The upper limit of q is about 0.2 Å^{-1} for all the measurements. This q limit is of the size range of the monomers, either the DGEBA or the D-230 diamine. Earlier work with partially deuterated DGEBA cured with D-230 diamine revealed a scattering peak at 0.37 Å^{-1} which corresponds to the average size of the monomers[24]. Accordingly, one does not expect to observe any fractal behaviour over a size scale smaller than the monomer, or equivalently the q range of interest in this work is expected to be below 0.37 Å^{-1}. As to the lower q limit, it depends solely on the Z average of the cluster size. The highest value of R_Z observed in this work is about 130 Å according to *Figures 4* and *6*, which corresponds to $q=0.05$ Å^{-1}. With the method used in the present work we cannot obtain any sample of higher value of p or R_Z without getting into the gelation region. Had a technique been available to extract epoxy samples with much smaller values of ε, the corresponding R_Z could have been in the micrometre range. In that circumstance, the suitable scattering measurements would be light scattering instead of neutron or X-ray scattering.

CONCLUSIONS

The crosslinking of epoxies in bulk using triamines as curing agents seems to follow the prediction of percolation theory as judged from the exponent relating the values of N_w and R_Z. This notion is believed to be true for the cure of epoxies via any polyaddition type of reaction. However, when a diamine is used as the curing agent, the substitution effect of the secondary amino group tends to alter the reaction towards that of FS type.

REFERENCES

1 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953
2 Stockmayer, W. H. *J. Chem. Phys* 1943, **11**, 45; 1944, **12**, 125
3 Gordon, M. and Ross-Murphy, S. B. *Pure Appl. Chem.* 1975, **43**, 1
4 Stauffer, D., Coniglio, A. and Adam, M. *Adv. Polym. Sci.* 1982, **44**, 103
5 Family, F. *J. Phys (A)* 1980, **13**, L325
6 deGennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, NY, 1979
7 Burchard, W. *Adv. Polym. Sci.* 1983, **48**, 1
8 Schaefer, D. W. and Keefer, K. D. *Phys. Rev. Lett.* 1984, **53** (14), 1383
9 Dusek, K. 'Developments in Polymerization 3', Applied Science Publishers, London, 1982, p. 143
10 Schmidt, M. and Burchard, W. *Macromolecules* 1981, **14**, 370
11 Schosseler, F. and Leibler, L. *Macromolecules* 1985, **18** (3), 398
12 Leibler, L. and Schosseler, F. *Phys. Rev. Lett.* 1985, **55** (10), 1110
13 Schaefer, D. W. and Keefer, K. D. 'Fractals in Physics', Elsevier Science Publishers, Amsterdam, 1986, p. 39
14 Daoud, M., Bouchaud, E. and Jannink, G. *Macromolecules* 1986, **19**, 1955
15 Bantle, S., Hasslin, H. W., Ter Merr, H. U., Schmidt, M. and Burchard, W. *Polymer* 1982, **23**, 1889
16 Chu, B., Wu, C., Wu, W. D. and Phillips, J. C. *Macromolecules* 1987, **20** (10), 2642
17 Ord, G. and Whittington, S. G. *J. Phys. (A)* 1982, **15**, L29
18 Rozenberg, B. A. *Adv. Polym. Sci.* 1985, **75**, 113
19 Zimm, B. H. and Stockmayer, W. H. *J. Chem. Phys.* 1949, **17**, 1301
20 Daoud, M., Family, F. and Jannink, G. *J. Physique Lett.* 1984, **45**, L99
21 Martin, J. E. and Ackerson, B. J. *Phys. Rev. (A)* 1985, **31** (2), 1180
22 Herrmann, H. J., Landau, D. P. and Stauffer, D. *Phys. Rev. Lett.* 1982, **49** (6), 412
23 Bansil, R., Willings, M. and Herrmann, H. J. *J. Phys. (A)* 1986, **19**, L1209
24 Wu, W.-L. and Bauer, B. J. *Polymer* 1986, **27**, 169