

Table I
Fractal Dimension (d_f) and Coil Behavior over Different K Ranges Based on the Epoxy Polymer Solution Scattering Curve in Figure 2

x^{-1} , Å	d_f^a for $y^{-1} =$				
	50 Å	40 Å	30 Å	20 Å	10 Å
R_g	2.01 ± 0.04	2.04 ± 0.03	2.03 ± 0.02	1.97 ± 0.02	1.94 ± 0.04
$R_g/2$	2.17 ± 0.03	2.16 ± 0.02	2.18 ± 0.01	2.17 ± 0.01	2.12 ± 0.02
$R_g/3$	2.18 ± 0.04	2.17 ± 0.02	2.20 ± 0.01	2.16 ± 0.01	2.10 ± 0.02
coil behavior ²² $I(K) \sim K^{-\beta}$					
	$y < K < 1/3$ (Å ⁻¹)			$y < K < 1/4$ (Å ⁻¹)	
y , Å ⁻¹	$1/30$	$1/20$	$1/10$	$1/30$	$1/20$
β	1.69 ± 0.06	1.62 ± 0.07	1.58 ± 0.09	1.74 ± 0.05	1.68 ± 0.06
	$1/10$			$1/10$	
					1.65 ± 0.10

^a fractal dimension, $I(K) \sim K^{-d}$ with $x < K < y$; the uncertainties presented here are standard deviations which increase over larger K ranges because of deviations from the power-law dependence.

with λ and θ being the X-ray wavelength and the scattering angle, respectively. In our case, we want to investigate branched epoxy polymers as self-similar fractal aggregates, which are indeed covalent-bonded molecular clusters created at each individual catalytic center, proceed to become larger branched epoxy polymer particles, and finally overlap with one another at the gelation threshold. Beyond the gel point, more cross-linking takes place for the epoxy polymer network to finally form a glass of relatively uniform optical homogeneity. In principle, at small scattering angles ($KR_g < 1$), light scattering, SAXS, or small-angle neutron scattering (SANS) measurements of the epoxy polymer solution permit determination of the weight-average molecular weight M_w and R_g of the macromolecular clusters formed. Here, we shall be concerned mainly with eq 2.

The epoxy monomers, the curing agent, and the catalyst used were 1,4-butanediol diglycidyl ether (DGEb) *cis*-1,2-cyclohexanedicarboxylic anhydride (CH), and benzyl dimethyl amine (CA), respectively. Purified and filtered components of the mixture in a molar ratio of DGEb:CH:CA = 1:2:0.001 were reacted at 80 °C and 1 atm. DGEb is known to link through CH in an alternating way and the polymerization reaction is initiated at the catalytic center. Aliquots of the reaction mixture consisting of branched alternating copolymers and the unreacted DGEb, CH, and CA could be withdrawn for analysis during the course of the polymerization process. The gel point was reached in about 2 days after ~47% conversion of the curing agent CH. SAXS measurements were performed on 10^{-3} – 10^{-2} g of the reaction mixture dissolved in 10 mL of methyl ethyl ketone (MEK). MEK acts as the main solvent component. The unreacted DGEb, CH, and CA are miscible with MEK.

Small-angle X-ray scattering data were collected by using a modified Kratky block-collimation small-angle X-ray diffractometer (SAXD)¹⁸ adapted for synchrotron radiation at the SUNY beamline, NSLS, Brookhaven National Laboratory (BNL), which provides a flux of $\sim 3 \times 10^{11}$ photons/s in a 0.9×0.6 mm focal spot.¹⁹ Thus, with our SAXD X-ray, we were able to reach $\theta \sim 1$ mrad corresponding to $K \sim 0.004$ Å⁻¹ (or a Bragg spacing of 1500 Å) using an incident slit width of 0.5 mm and $\lambda = 1.54$ Å. It should be noted that the synchrotron source is tunable, permitting even a broader K -range. The wavelength tunability has also made anomalous scattering another powerful feature of our SAXS instrumentation. In addition, the high X-ray flux provides sufficient intensity for time-resolved work. A K -range of close to 70-fold without moving the linear position sensitive detector was achieved.

Figure 1 shows log-log plots of time evolution of scattered X-ray intensity (I) as a function of K with $\lim_{K \rightarrow 0} (I/CH)^{1/2} = M_w$. C is the concentration and H' is an

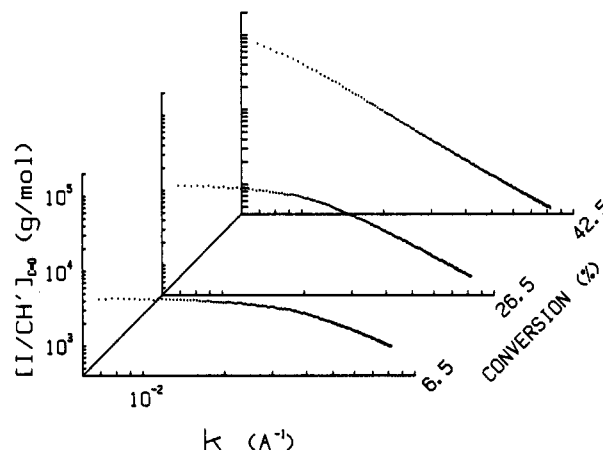


Figure 1. log-log plots of scaled absolute excess scattered X-ray intensity $(I/CH)^{1/2}$ as a function of K at three different stages of the epoxy polymerization process before the gel point (~47% CH conversion). DGEb:CH:CA = 1:2:0.001 at 80 °C and 1 atm. H' is a scaled instrument constant and C is the concentration. In the limits $C \rightarrow 0$ and $K \rightarrow 0$, I/CH' denotes the molecular weight of the branched epoxy polymer in grams per mole. Only a portion (187 data points) of each scattering curve is plotted.

instrument constant, calibrated by using absolute light scattering data. The subscript $C = 0$ denotes the values at infinite dilution. We used light scattering results on intermolecular interactions to correct for the SAXS data measured at finite concentrations. During epoxy polymer formation, the initial slope from SAXS measurements can be related to R_g if $KR_g < 1$. According to Figure 1, the power-law fractal behavior for $I(K)$ covers a fairly short K -range during the early stages of epoxy polymer formation. As the polymerization reaction progresses, the fractal power-law region in Figure 1 extends toward lower K values because R_g of the branched epoxy molecular cluster increases with the polymerization reaction. Near the gel point (~47% CH conversion), R_g becomes quite large and a substantial portion of the SAXS range obeys eq 2. Figure 2 shows a more complete representative scattering curve starting at $KR_g < 1$ and ending at $K\xi > 1$. At $KR_g < 1$, the initial slope denotes a measurement of the radius of gyration. At $K\xi > 1$, the slope is related to the coil behavior of polymer chains between cross-linking points. The fractal dimension d_f of the branched epoxy polymer in MEK and in the presence of a small amount of unreacted DGEb, CH, and CA has been determined over different ranges of K with values listed in Table I.

We note that the measured value of d_f ($=2.17 \pm 0.03$) for $2/R_g < K < 1/30$ Å⁻¹ near the gelation threshold²⁰ in a fairly good solvent (MEK) with $A_2 \sim 3.6 \times 10^{-4}$ mL mol/g² differs from $d_f = 4$, Zimm-Stockmayer²¹ (Cayley tree); $d_f = 2.5$, for diffusion limited aggregation; and $d_f =$

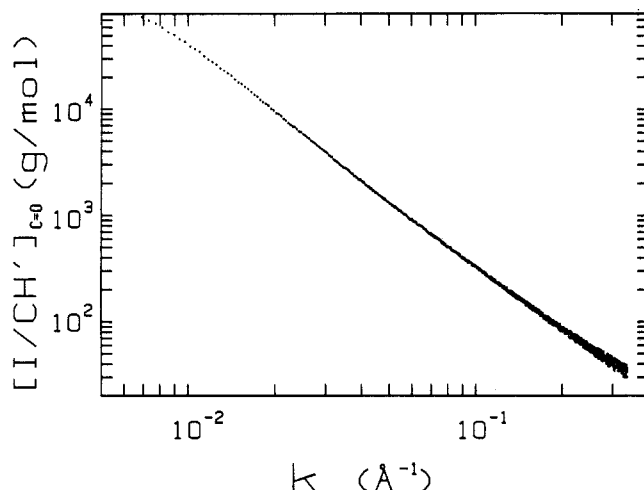


Figure 2. log-log plot of a representative scattering curve with 816 data points at 42.5% CH conversion. The X-ray scattering intensity has been corrected for nonlinear response of the linear position sensitive detector (LPSD), stray X-ray, solvent background, and sample transmission. Desmearing was not needed because of the small collimated synchrotron beam cross section ($\sim 0.5 \text{ mm} \times 1 \text{ mm}$). A K range of close to 70-fold could be achieved without moving the LPSD. Least-squares fitting of eq 2 over different K ranges is listed in Table I. $\langle R_g^2 \rangle_z^{1/2} = 191 \text{ \AA}$ and $M_w = 1.42 \times 10^5 \text{ g/mol}$.

1.75, for cluster-cluster aggregation but more closely agrees with the prediction of Daoud and Joanny²² on the conformation of branched polymers ($d_f = 4(d+1)/7 = 2.285$) in a Θ solvent and with experimental results for colloidal aggregates³ (2.12 ± 0.05).

Over a limited range of K ($1/20 \lesssim K \lesssim 1/3$ (or $1/4 \text{ \AA}^{-1}$) where we have essentially set a correlation length ξ of $\sim 20 \text{ \AA}$ and an estimated segment size a of $\sim 3\text{--}4 \text{ \AA}$, a β value of 1.65 ± 0.07 is estimated, while Daoud and Joanny²² predicted a linear blob behavior of $\beta \sim 5/3$ for the branched polymer chains between cross-linking points.

From our SAXS results, we can draw the following conclusions: 1. We can use SAXS to determine d_f which is related to the epoxy polymer structure. 2. Before the gelation threshold, we can determine M_w and R_g using static scattering techniques. With d_f and eq 1 and a knowledge of the ratio of R_g and the hydrodynamic radius (R_h) as a function of molecular weight, the molecular weight distribution at each stage of the polymerization process can be obtained experimentally from dynamic light scattering, especially in view of the fact that the particle scattering factor in the visible range for such epoxy systems is near unity. Finally, we suggest that 3. Beyond the gelation threshold, we can use fractal dimension to investigate changes in epoxy structure.

A detailed study of the structure and dynamics of this epoxy model system using a combination of SAXS and

light scattering is under way.

Acknowledgment. We gratefully acknowledge support of the epoxy project by the U.S. Army Research Office (DAAG 2985 K0067), the SAXS instrumentation by the Department of Energy (DEFG0286ER45237A001) and the U.S. Army Research Office, and the use of the SUNY beam line supported by the Department of Energy (DEFG0286ER45231A001).

Registry No. DGEB (homopolymer), 29611-97-0; CH, 85-42-7.

References and Notes

- (1) Mandelbrot, B. *Fractals, Form, Chance and Dimension*; Freeman: San Francisco, 1977.
- (2) Stanley, H.; Reynolds, P.; Redner, S.; Family, F. *In Real Space Renormalization*; Burkhardt, T. W., van Leeuwen, J. M. J., Eds.; Springer: New York, 1982; Chapter 7.
- (3) Schaefer, D. W.; Martin, J. E.; Wiltzius, P.; Cannell, D. S. *Phys. Rev. Lett.* **1984**, *52*, 2371.
- (4) Martin, J. E.; Schaefer, D. W. *Phys. Rev. Lett.* **1984**, *53*, 2457.
- (5) Wiltzius, P. *Phys. Rev. Lett.* **1987**, *58*, 710.
- (6) Schaefer, D. W.; Keefer, K. D. *Phys. Rev. Lett.* **1984**, *53*, 1383.
- (7) Chambon, F.; Winter, H. H. *Polym. Bull. (Berlin)* **1985**, *13*, 499.
- (8) Muthukumar, M.; Winter, H. H. *Macromolecules* **1986**, *19*, 1284.
- (9) Feder, J.; Jossang, T. *Phys. Rev. Lett.* **1984**, *53*, 1403.
- (10) Weitz, D. A.; Huang, J. S.; Lin, M. Y.; Sung, J. *Phys. Rev. Lett.* **1985**, *54*, 416.
- (11) Witten, T. A.; Sander, L. M. *Phys. Rev. Lett.* **1981**, *47*, 1400.
- (12) Meakin, P. *Phys. Rev. Lett. A* **1983**, *27*, 604, 1495.
- (13) Kaufman, J. H.; Baker, C. K.; Nazzari, A. I.; Flickner, M.; Melroy, O. R. *Phys. Rev. Lett.* **1986**, *56*, 1932.
- (14) Family, F. *In Random Walks and Their Applications in the Physics and Biophysical Sciences—1982*; Schlesinger, M. F., West, B. J., Eds.; AIP Conference Proceedings No. 109; American Institute of Physics: New York, 1984; p 33.
- (15) Meakin, P. *Phys. Rev. Lett.* **1983**, *51*, 1119.
- (16) Kolb, M.; Botet, R.; Jullien, J. *Phys. Rev. Lett.* **1983**, *51*, 1123.
- (17) Hentschel, H. G. E.; Deutch, J. M. *Phys. Rev. Lett. A* **1984**, *29*, 1609.
- (18) Chu, B.; Wu, D.-Q.; Wu, C. *Rev. Sci. Instrum.* **1987**, *58*, 1158.
- (19) Phillips, J. C.; Baldwin, K. S.; Lehnert, W. F.; Leamand, A. D.; Prewitt, C. T. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1986**, *246*, 182.
- (20) Stauffer, D.; Coniglio, A.; Adam, M. *Adv. Polym. Sci.* **1982**, *44*, 74.
- (21) Zimm, B.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
- (22) Daoud, M.; Joanny, J. F. *J. Phys.* **1981**, *42*, 1359.

Benjamin Chu,* Chi Wu, and Dan-qing Wu

Chemistry Department
State University of New York at Stony Brook
Long Island, New York 11794-3400

James C. Phillips

Chemistry Department
State University of New York at Buffalo and
SUNY X3 Beamline, NSLS, Bldg. 725
Brookhaven National Laboratory
Upton, New York 11973

Received May 14, 1987;

Revised Manuscript Received July 20, 1987