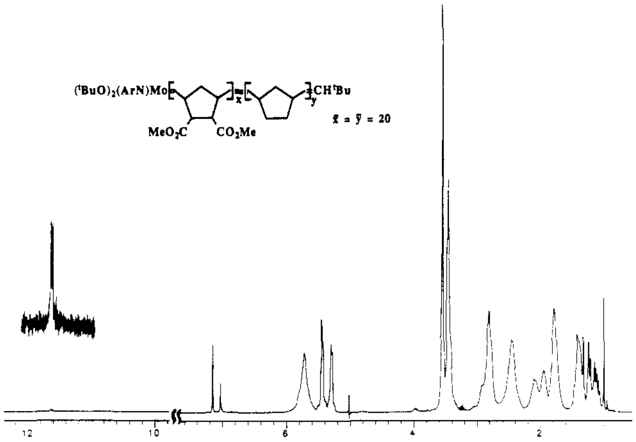

Figure 2. ^{1}H NMR spectrum of a sample of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ after addition of 20 equiv of norbornene followed by 20 equiv of *endo,endo*-5,6-dicarbomethoxynorbornene.

The results of two critical experiments are shown as the last two entries in Table I. Living copolymers were prepared via the sequential addition of 50 equiv of DCNBE and 200 equiv of NBE (and vice versa) to 1 over a period of ~15 min, cleaved off with benzaldehyde, and characterized in the standard manner.[5] The number-average molecular weights and the polydispersities of the two block copolymers are virtually identical. (The slightly higher M_n and polydispersity in the 50/200 block could be ascribed to a small amount of destruction of alkylidene catalyst centers since chain-propagating species are exposed to ester for a longer period.) Therefore no significant amount of catalyst is destroyed in either experiment, and we must conclude on the basis of these and the results described above that at least 100 equiv of ester functionality (in 50 equiv of monomer) is tolerated absolutely on the time scale of a typical experiment (15 min).

To our knowledge this is the first report of a controlled polymerization of a norbornene that is derivatized with a relatively reactive functionality. We believe these results have important practical implications for the preparation of functionalized homopolymers and block copolymers and are in the process of determining what other functionalities can be tolerated. These results also point out that differences in reactivity between analogous molybdenum and tungsten alkylidene complexes can be relatively important from the practical point of view of being able to prepare low polydispersity polymers.

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(5) All reactions were performed under an atmosphere of dinitrogen. A standard reaction consisted of adding the monomer dissolved in 7–10 mL of toluene dropwise over 5 min to a vigorously stirred solution of 10 mg of 1 in 25 mL of toluene. Stirring was continued for 5 min and then 10 μL of benzaldehyde was added in order to cleave off the polymer through a Wittig-like reaction (confirmed by ^{1}H NMR to be complete in seconds, even at these low concentrations). The solution was then concentrated to 10 mL and the polymer precipitated by addition of 50 mL of methanol containing ~1% 2,6-di-*tert*-butyl-4-methylphenol (BHT) as an antioxidant. The polymer was collected, dried in vacuo, and analyzed by standard gel permeation chromatography in toluene on a Waters 150C instrument equipped with three styragel columns calibrated with polystyrene standards. A single, smooth, symmetrical peak was observed in all cases. Very occasionally a small amount (~5%) of a relatively high molecular weight material was observed. It was not included in the dispersity calculations. Similar sporadic high molecular weight polymer was observed also in the tungsten-based system.[3] The high molecular weight material has not yet been identified. The possibility that it is an artifact cannot be excluded.

(6) If one assumes that the rate of propagation equals the rate of initiation, then addition of 1 equiv of monomer should leave only 37% of 1 behind.[7] The difference in rate of propagation versus rate of initiation evidently is not great enough to raise significantly the polydispersity of polymers containing more than 50 equiv of monomer.

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(8) Kinetic studies at low temperatures confirm these proposals. Full details will be reported in due course.

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Fractal Geometry in Branched Epoxy Polymer Kinetics

The concept of fractal geometry[1,2] has shown to be a useful approach to describe the structure of random systems, such as aggregates of colloidal silica,[3–5] branched silica condensation polymers,[6] cross-linked poly(dimethylsiloxane),[7,8] aggregating proteins,[9] and gold colloids,[10] as well as diffusion-limited[11,12] polymerization of the conducting polymer polypyrrole[13] and other growth processes (e.g., pecolation[14] and cluster–cluster aggregation[15–17]). The two salient features of the new fractal concept, i.e., to describe random structures in terms of fractal dimension and to use fractal dimension to investigate polymerization kinetics, should be applicable to investigations of even more complex systems, such as epoxy network formation and polymerization kinetics. In this paper, we want to report preliminary time-resolved small-angle X-ray scattering (SAXS) measurements of epoxy clusters before their gelation threshold using the State University of New York (SUNY) beam line at the National Synchrotron Light Source (NSLS).

The fractal dimension d_f of a molecular cluster with mass M and radius of gyration R_g has the relation

$$M \sim R_g^{d_f} \qquad (1)$$

Equation 1 applies only for distances small compared to R_g and large compared to a length related to the distance between entanglement points ξ. The corresponding static structure factor $S(K)$ (~the scattered intensity I), which is the Fourier transform of the pair correlation function, has a power-law relation

$$S(K) \sim K^{-d_f} \qquad (2)$$

in the range $KR_g \gg 1 \gg K\xi$ where $K = (4\pi/\lambda)\sin(\theta/2)$

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

	$d_f{}^a$ for y^{-1} =				
x^{-1}, Å	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}	$^1/_{30}$	$^1/_{20}$	$^1/_{10}$	$^1/_{30}$	$^1/_{20}$	$^1/_{10}$
β	1.69 ± 0.06	1.62 ± 0.07	1.58 ± 0.09	1.74 ± 0.05	1.68 ± 0.06	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 ~3 × 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.

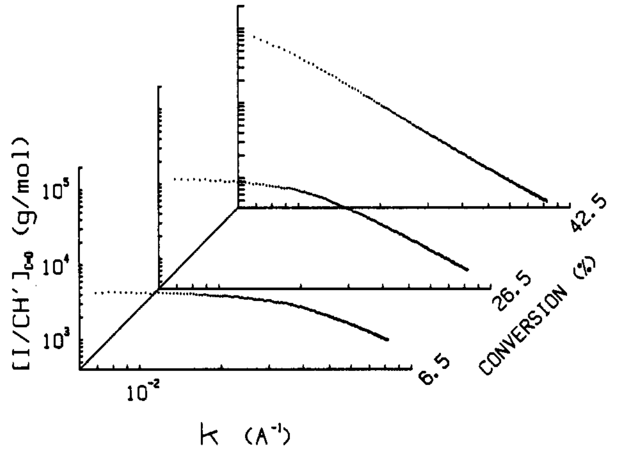

Figure 1. log–log plots of scaled absolute excess scattered X-ray intensity $(I/CH')_{C=0}$ as a function of K at three different stages of the epoxy polymerization process before the gel point (~47% CH conversion). DGEB:CH:CA = 1:2:0.001 at 80 °C and 1 atm. H' is a scaled instrument constant and C is the concentration. In the limits $C \to 0$ and $K \to 0$, 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.

Figure 1 shows log–log plots of time evolution of scattered X-ray intensity (I) as a function of K with $\lim_{K\to 0} (I/CH')_{C=0} = M_w$. C is the concentration and H' is an 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 ± 0.03) for $2/R_g < K < 1/30$ Å^{-1} near the gelation threshold[20] in a fairly good solvent (MEK) with $A_2 \sim 3.6 \times 10^{-4}$ mL mol/g^2 differs from $d_f = 4$, Zimm–Stockmayer[21] (Cayley tree); $d_f = 2.5$, for diffusion limited aggregation; and d_f =

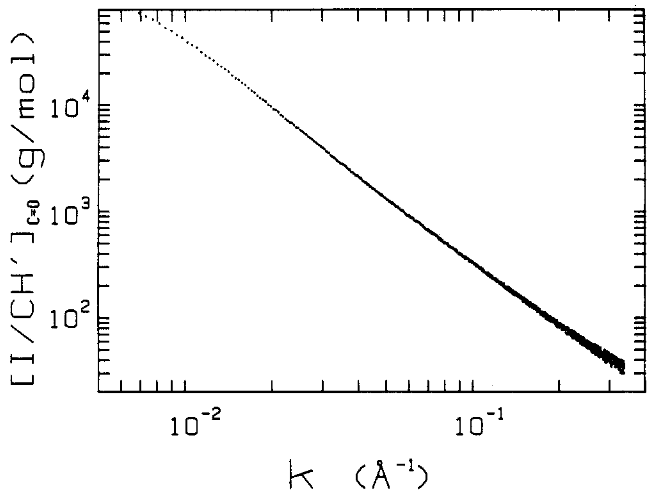

Figure 2. log–log plot of a representative scattering curve with 816 data points at 42.5% CH conversion. The X-ray scattering intensity has been corrected for nonlinear response of the linear position sensitive detector (LPSD), stray X-ray, solvent background, and sample transmission. Desmearing was not needed because of the small collimated synchrotron beam cross section (~0.5 mm × 1 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. $\langle R_g^2 \rangle_z^{1/2} = 191$ Å and $M_w = 1.42 \times 10^5$ g/mol.

1.75, for cluster–cluster aggregation but more closely agrees with the prediction of Daoud and Joanny[22] on the conformation of branched polymers ($d_f = 4(d + 1)/7 = 2.285$) in a Θ solvent and with experimental results for colloidal aggregates[3] (2.12 ± 0.05).

Over a limited range of K ($^1/_{20} \lesssim K \leq {}^1/_3$ (or $^1/_4$ Å^{-1}) where we have essentially set a correlation length ξ of ~20 Å and an estimated segment size a of ~3–4 Å, a β value of 1.65 ± 0.07 is estimated, while Daoud and Joanny[22] 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.

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

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