(1994); H. S. Zhou, H. Sasahara, I. Honma, H. Komiyama, *ibid.*, p. 1534; B. O. Dabbousi, C. B. Murray, M. F. Rubner, M. G. Bawendi, *ibid.*, p. 216.
4. L. Shieh, Y. Tamada, A. Domb, R. Langer, *J. Controlled Release* **29**, 73 (1994); R. Gref *et al.*, *Science* **263**, 1600 (1994); R. Langer, *Acc. Chem. Res.* **26**, 537 (1993).
5. M. Granström, M. Berggren, O. Inganäs, *Science* **267**, 1479 (1995).
6. F. T. Wallenberger, *ibid.*, p. 1274 (1995).
7. C. B. Gorman, H. A. Biebuyck, G. M. Whitesides, *Chem. Mater.* **7**, 252 (1995); R. Singhvi *et al.*, *Science* **264**, 696 (1994).
8. C. Liu, H. Pan, M. A. Fox, A. J. Bard, *Science* **261**, 897 (1993).
9. D. Noble, *Anal. Chem.* **67**, 201A (1995); S. P. A. Fodor *et al.*, *Science* **251**, 767 (1991).
10. M. Yan, S. X. Cai, M. N. Wybourne, J. F. Keana, *J. Am. Chem. Soc.* **115**, 814 (1993); L. F. Rozsnyai, D. R. Benson, S. P. A. Fodor, P. G. Schultz, *Angew. Chem. Int. Ed. Engl.* **31**, 759 (1992).
11. Y. Chigusa, K. Fujiwara, Y. Hattori, Y. Matsuda, *Optoelectronics* **1**, 203 (1986); M. Mogi and K. Yoshimura, *Proc. Soc. Photo-Opt. Instrum. Eng.-Int. Soc. Opt. Eng.* **1067**, 172 (1989).
12. K. S. Bronk and D. R. Walt, *Anal. Chem.* **66**, 3519 (1994); S. M. Barnard and D. R. Walt, *Nature* **353**, 338 (1991).
13. A typical hydrophobic polymerization solution contained 500 μl (15 to 20% acryloxypropyl-methylsiloxane) (80 to 85% dimethylsiloxane) copolymer (Gelest, Tullytown, PA), 30 mg of benzoin ethyl ether (Aldrich), and 1000 μl of dichloromethane (Fisher). A typical hydrophilic polymerization solution contained 1 ml (5% ethylene glycol dimethacrylate, 95% *N*-vinyl pyrrolidone) of monomer (Aldrich), 60 mg of benzoin ethyl ether, and 1 ml of phosphate buffer (pH 7).
14. The light flux for deposition was 18.8 mW/cm^2, and the polymerization time was 1.5 s.
15. Measurements were obtained by atomic-force microscopy with a Digital Instruments Dimension 3000 scanning probe microscope. Microstructures on imaging fibers were analyzed in the tapping mode, whereas the microstructure on the glass substrate was analyzed in the contact mode.
16. B. G. Healy and D. R. Walt, unpublished results.
17. We gratefully acknowledge NIH (grant GM 48142) and the U.S. Department of Energy for financial support. The authors also would like to thank F. P. Milanovich, J. Richards, and S. Brown of Lawrence Livermore National Laboratories for their help in the design and fabrication of the polymer deposition system and Galileo Electro-Optics Corporation for the gift of imaging fiber.

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Self-Condensing Vinyl Polymerization: An Approach to Dendritic Materials

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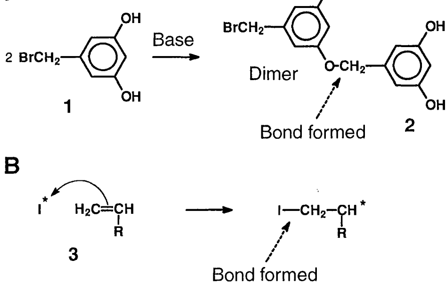
Self-condensing vinyl polymerization was used to produce dendritic polymers with both highly branched structures and numerous reactive groups. A vinyl monomer will undergo self-polymerization if it contains a pendant group that can be transformed into an initiating moiety by the action of an external stimulus. The self-polymerization combines features of a classical vinyl polymerization process with those of a polycondensation because growth is accomplished by the coupling of reactive oligomers. Highly branched, irregular dendritic structures with a multiplicity of reactive functionalities are obtained by polymerization of 3-(1-chloroethyl)-ethenylbenzene.

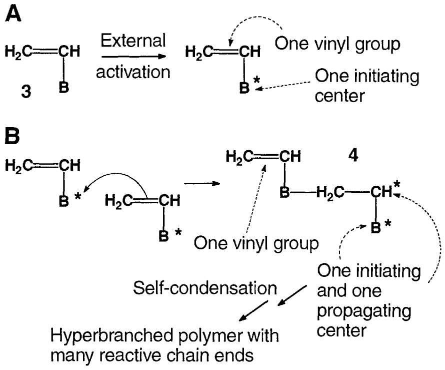
The polymerization of vinyl monomers remains one of the most heavily used organic processes, and millions of tons of polymers are produced by this route every year. Despite increased sophistication in the design of catalysts, and the ability to better regulate growth processes, sequences of monomers, or the chain ends of polymers, "linear" propagation is the usual method of producing a relatively limited array of polymer architectures. The development of new polymer architectures is an important target because it is soon followed by findings of new properties and applications (*1*). For example, the globular shape of three-dimensional polymers such as dendrimers makes them attractive in applications ranging from catalysis to drug delivery systems. However, regular dendrimers are accessible only through multistep syntheses that limit their availability (*1*, *2*). Less regular, hyperbranched polymers are more accessible, but their preparation has been restricted to the polycondensation of AB_2 monomers (*3*–*5*).

We now report a versatile approach to the production of highly branched polymer architectures in which a type of vinyl polymerization is encountered that proceeds with features normally associated with polycondensation reactions. The fundamental premise of our approach, in which an AB vinyl monomer is used to prepare a highly branched polymer, is contrasted with that in which an AB_2 monomer such as **1** is used to produce a hyperbranched polyether (Schemes 1 and 2). Williamson etherification of the benzylic bromide group A of **1** with one of the phenolic groups B of another monomer unit yields the dimer **2** (Scheme 1). The overall growth process involves two monomers containing a total of six potential reactive centers (2A + 4B) and gives rise to a dimer with only four remaining reactive centers (1A + 3B). Therefore, bond formation consumes two reactive centers (one A and one B), whereas the newly formed ether bond is incapable of participation in any further growth process. In the case of the AB vinyl monomer **3**, in which A is a vinyl group and B is a pendant group (for example, the aromatic ring of styrene), the polymerization is started by an activated initiating moiety, I*. Depending on the type of polymerization, I* could be a "living" free radical, an electrophilic cationic moiety, or a carbanion. In addition, reaction of I* with one carbon atom of the double bond (DB) results in the consumption of two reactive centers with concurrent formation of a bond that is usually incapable of further reaction. However, the process also creates a new active site on the second carbon atom of the DB (Scheme 1) that is capable of reacting with yet another DB in the process of propagation. Because the DB behaves as an effective difunctional moiety, the foundation may be laid for growth of highly branched structures through appropriate manipulations of the pendant group B.

Scheme 2 outlines the basic concept of self-condensing vinyl polymerization. The AB vinyl monomer **3** is now selected with a



Scheme 1. (**A**) Typical polycondensation process. Addition does not create any new reactive centers. (**B**) Typical vinyl polymerization process. Addition creates a new reactive center.



Scheme 2.

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B group that may be activated by an external stimulus to a B* moiety that itself is capable of initiating the polymerization of a vinyl monomer (for example, by means of radical or cationic processes). The polymerization process is initiated by reaction of one initiating B* group with the DB A of another AB* monomer unit to yield the dimer **4** (Scheme 2). The reaction creates a new reactive center capable of propagation and the dimer now has one DB, one "initiating" B* center, and one propagating center. Because both the initiating B* and the newly created propagating center have essentially the same reactivity—both react in the same way with a vinyl group—the AB monomer has effectively been transformed into an AB_2-type monomer that is known to give rise to hyperbranched structures (*3–5*). Additional condensations involving the activated AB* monomer, dimer **4**, and (eventually) larger oligomeric species produced by subsequent condensations gives rise to a highly branched high molecular weight polymer.

We have termed this polymerization process self-condensing vinyl polymerization because it operates by the repeated stepwise coupling of growing moieties with each other, using steps typically observed in classical vinyl polymerizations. The polymerization is therefore a hybrid of classical polycondensations and vinyl polymerizations. In principle, this concept may be applied to numerous vinyl polymerization mechanisms, depending on the nature of the B group and of the external stimulus that is applied. The activation step may involve an external additive or the application of heat or light. For example, B may be activated by the action of a Lewis acid to yield an electron-poor initiating moiety that reacts with A through a "living" carbocationic mechanism (see below). Alternatively, B might be activated to a "living" free radical (*6*) that again would react with A.

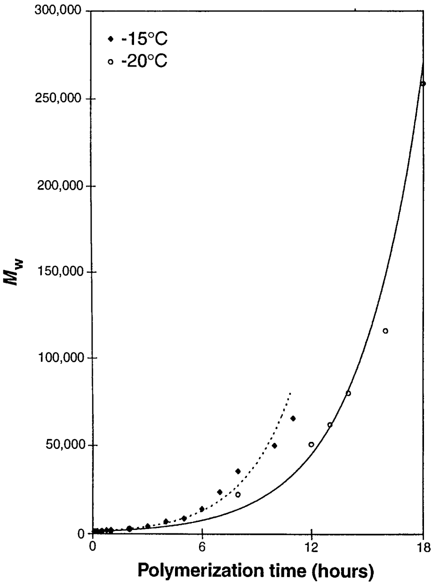


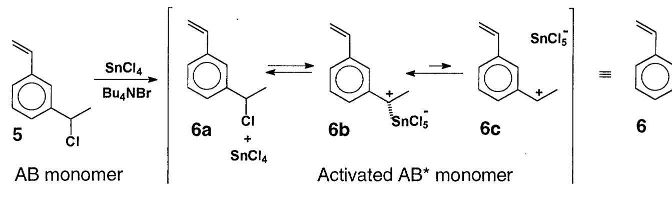
Fig. 1. Dependence of the weight-average molecular weight ($\bar{M}_w$) of the polymers formed on the polymerization time.

We have now demonstrated the concept with the polymerization of a styrenic monomer, 3-(1-chloroethyl)-ethenylbenzene. Mechanistically, the coupling reaction is based on findings reported for the "living"-like polymerization of styrene (*7*, *8*). In this process, styrene is polymerized with 1-chloroethylbenzene as the latent initiator that is activated by addition of stannic chloride. The polymerization involves rapid exchange between active (cationic) and dormant (benzylic halide and Lewis acid) species. To obtain more regular, low-dispersity polymers, we added a tetrabutylammonium halide to reduce the lifetime of the active ion pairs.

The AB monomer, 3-(1-chloroethyl)-ethenylbenzene (**5**), incorporates both the polymerizable DB of styrene (A group) and the latent initiator moiety of 1-chloroethylbenzene (B group). Monomer **5** is obtained by addition of one molecule of HCl to commercial, high-grade divinylbenzene at −30°C (*9*). The reaction mixture is then purified by vacuum distillation and flash chromatography. The monomer usually contains some of the 4-chloroethyl isomer that cannot be separated readily, but this does not affect the outcome of the subsequent polymerization. The polymerizations are carried out in dry dichloromethane under nitrogen by rapid addition of the chilled monomer to a mixture of the activator, $SnCl_4$, and the added salt, tetrabutylammonium bromide (*10*).

The kinetics of the polymerization were observed at two temperatures, −15° and −20°C (Fig. 1). As expected, a decrease in temperature slowed the reaction rate and allowed monitoring of the formation of higher relative molecular mass (M_r) polymers. The time-dependence profile of the molecular weights resembled that of a typical polycondensation; an initial period of slow chain growth (up to 4 to 5 hours) was followed by a period of exponential increase of the molecular weights. The polydispersity of the polymers obtained also increased as the polymerization proceeded, thereby deviating from the values typically encountered in a polycondensation system (the ratio of the weight-average and number-average molecular weights, $M_w/M_n \geq 6$, whereas M_w/M_n approaches 2 in classic polycondensation). Although such high polydispersities are commonly observed with other hyperbranched polymers obtained by classical polycondensations (*5*), the mechanism of polymer growth is obviously complex. The activated monomer AB* itself is a mixture (*11*) of species such as **6a**, **6b**, and **6c** in rapid equilibrium (Scheme 3). Previous studies with styrene (*7*, *8*) have shown that because of the added salt, the equilibrium does not favor highly reactive free-ionic species with long lifetimes (such as **6c**). Instead, the actual initiating ion pair has a short lifetime and collapses rapidly to the dormant covalent species, **6a**. To simplify the schematic representation of the stepwise growth process that actually takes place, we represent the activated AB* monomer by structure **6**. Therefore, two molecules of **6** can couple to form a dimer, **7** (Scheme 4). Further growth by reaction of either the propagating or the initiating site of **7** with **6**, or with itself, would produce trimers **8a** and **8b** and tetramers **9a** and **9b** (Scheme 4). Because of the multiplicity of latent carbocationic sites on these moieties, further growth can proceed, yielding both linear or hyperbranched oligomers. All of the growing macromolecules contain both initiating and propagating sites that are subject to the same rapid equilibria between active and dormant states (*8*) as outlined for **6**. Although some sites may be less hindered than others, all are secondary benzylic and have a similar reactivity. Therefore, growth is expected to be near statistical, resulting in branched high molecular weight products.

Side reactions such as the cyclization of oligomers (*12*) likely contribute to the broadening of the molecular weight distribution and the formation of looped branches in the final polymer. However, the presence of several reactive sites in each growing molecule allows even the cyclic moieties that may be formed to participate in further growth, in sharp contrast to the back-biting reactions that terminate classical ionic polymerizations. Termination by quenching with methanol, followed by an



Scheme 3

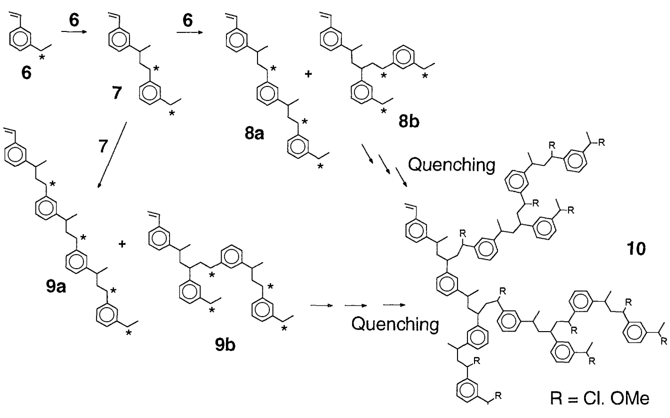
acid wash to remove the large amount of Lewis acid, yields a final polymer with an irregular, branched structure (**10**) that incorporates numerous chloride, methoxy, and other end groups, and with a molecular weight >100,000 (Table 1).

Close monitoring of the polymerization by size exclusion chromatography (SEC) in the initial stages of the propagation process supports the self-condensing vinyl polymerization mechanism (Scheme 4). Figure 2, A and B, shows the SEC chromatograms representative of the composition of the whole reaction mixture at regular time intervals. For the first 45 min, the polymerization mixture consists mainly of oligomers with degrees of polymerization (DP) ranging from 2 to 7 (Fig. 2A). Surprisingly, the amount of trimer is very low compared to its higher molecular weight analogs, suggesting that the coupling of growing oligomers (that is, dimer-dimer and higher) is the major reaction pathway even after only 5 min of reaction. This doubling of molecular weight appears to be the major contributor to growth after 2 hours (Fig. 2B), in which each successive curve can be roughly correlated to this doubling phenomenon. It is likely that at later stages of the self-condensation, with the monomer and lower molecular weight oligomers already consumed, the reaction conditions are more favorable for statistical hyperbranching than for linear growth.

Table 1 shows the influence of the polymerization conditions on the molecular weight characteristics of the polymers formed. The addition of approximately equimolar amounts of the activator $SnCl_4$ to the monomer used in relatively high concentration results in the formation of high molecular weight polymers (Table 1, runs 2 to 4). Under other reaction conditions (runs 1, 5, and 6), the polymers that are obtained have lower M_r values. Consideration of the proposed mechanism of growth suggests that activation of a high percentage of the monomer units may be a prerequisite for the formation of high molecular weight products and a key factor for the hyperbranching pathway. However, under appropriate reaction conditions, the occurrence of fast exchange reactions can also result in the formation of hyperbranched products. As with the "living" polymerization of styrene (*7*, *8*), the addition of a tetrabutyl ammonium halide suppresses the formation of free carbocations and therefore contributes to slowing the reaction. Because of the paucity of vinyl groups available for growth in the latter stages of the polymerization, it may be expected that elimination side reactions resulting in disubstituted DBs could also contribute to the overall growth process or the formation of loops without causing gelation.

The polymer yields (Table 1) were obtained after a single precipitation into methanol. A classical Mark-Houwink-Sakurada (MHS) plot (Fig. 3) shows that the intrinsic viscosity ([η]) of the self-condensed polymers is lower than that of polystyrenes (PSt) of similar apparent M_r as measured by SEC. In addition, the slope of log [η] versus log M_r, in which each data point represents a separate polymer, is much lower than that for the linear polymer (MHS exponent α = 0.702 for PSt versus 0.430 for the polymer of **5**), which indicates a decreased level of interaction between solvent and polymer as is typically encountered in densely branched macromolecules. A similar finding (*5*) with data points obtained across a single M_r distribution was interpreted as an indication for the presence of a hyperbranched structure (*13*). Because the MHS plot (Fig. 3) was obtained with M_r's for the hyperbranched polymers, the value of the MHS exponent α is not absolute. This value should be considered as an upper limit for α, and more accurate determinations of the structural features of the hyperbranched polymers are being carried out with multiangle laser light scattering.

The marked difference observed in the M_r's calculated by conventional PSt calibration and "universal" calibration further supports the notion of hyperbranching in our polymers (*14*). For example, sample 2 (Table 1) has an M_r of 68,000 as deter-



Scheme 4

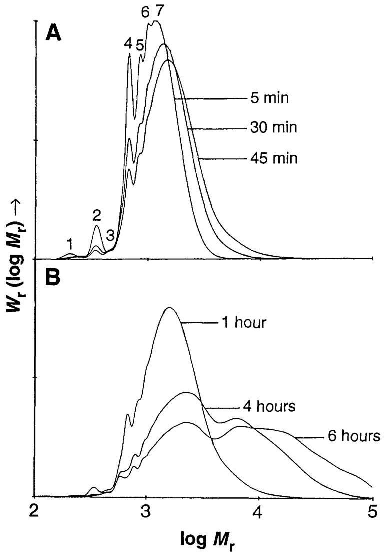


Fig. 2. Time dependence of the composition of the polymerization mixtures monitored by size exclusion chromatography [M_r is plotted versus the mass-sensitive detector response W_r (log M_r) in which W_r is the weight fraction at a particular M_r]. (**A**) Initial stage. The numbers of the peaks represent the degree of polymerization for the corresponding oligomers. (**B**) Later stages.

Table 1. Polymerization conditions and molecular weight characteristics of the materials formed. Solvent, CH_2Cl_2; $Bu_4N^+Br^-$, 40 mol% $SnCl_4$; temperature, −15° to −20°C. Gel-permeation chromatography (GPC) analyses were carried out in THF at 40°C on a set of four PL Gel columns with pore sizes 100, 500, and 1000 Å and mixed C. The eluent flow rate was 1 ml/min. The molecular weights were calculated with the use of polystyrene standards and universal calibration.

No.	Monomer **5** (M)	$SnCl_4$/**5**	Time (hours)	Yield (%)	Polystyrene standards			Universal calibration			[η] (dl/g)
					M_n (×10³)	M_w (×10³)	M_w/M_n	M_n (×10³)	M_w (×10³)	M_w/M_n	
1	0.35	0.3	24	89				4.9	33	6.6	0.056
2*	0.53	1.1	8	80	33	68	2.0	46	130	2.9	0.094
3*	0.53	1.1	10	89	32	120	3.7	50	250	5.1	0.170
4*	0.53	1.1	12	80	47	240	5.0	68	660	9.8	0.204
5	0.33	2.2	8	88				3.4	17	4.9	0.055
6	0.25	3.1	8	62				3.6	17	4.7	0.058

*GPC data were obtained from fractionated polymers with yields 41% (run 2), 60% (run 3), and 51% (run 4), respectively.

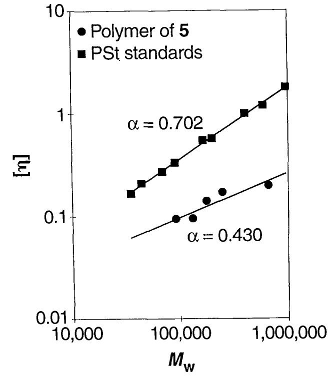


Fig. 3. Mark-Houwink-Sakurada plot for linear PSt standards and poly-**5** obtained in THF at 30°C.

mined by PSt standards, whereas the M_r of the same sample is twice as high when determined by the "universal" calibration method that is heavily dependent on a homogeneous density distribution across the entire macromolecule. This discrepancy increases with M_r (Table 1, runs 2 to 4).

Self-condensing vinyl polymerization may be broadly applicable to a large number of polymerization techniques and different AB monomer structures. We have succeeded in applying it to the preparation of hyperbranched polymers by the "living" free radical polymerization (*6*) of AB vinyl monomers. The versatility of the approach stems from the variety of architectures that may be obtained with the use of several monomers such as styrene and substituted styrenes to produce unusual polymer architectures in one pot reactions. For example, stars and linear-dendritic hybrid structures can be obtained by sequential addition of appropriately selected monomers. Given the interesting properties of these hybrid structures (*15*, *16*), a fast synthetic process for their preparation would be very beneficial.

REFERENCES AND NOTES

1. J. M. J. Fréchet, *Science* **263**, 1710 (1994); B. I. Voit, *Acta Polymer.* **46**, 87 (1995).
2. J. Issberner, R. Moors, F. Vögtle, *Angew. Chem. Int. Ed. Engl.* **33**, 2413 (1994); D. A. Tomalia and H. D. Durst, in *Top. Curr. Chem.* **165**, 193 (1993).
3. Y. H. Kim and O. W. Webster, *J. Am. Chem. Soc.* **112**, 4592 (1990).
4. L. J. Mathias and T. W. Carothers, *ibid.* **113**, 4043 (1991); C. J. Hawker, R. Lee, J. M. J. Fréchet, *ibid.*, p. 4583; V. Percec and M. Kawsumi, *Macromolecules* **25**, 3843 (1992); K. E. Uhrich, C. J. Hawker, J. M. J. Fréchet, S. R. Turner, *ibid.*, p. 4583; M. Suzuki, A. Ii, T. Saegusa, *ibid.*, p. 7071; E. Malmström, M. Johansson, A. Hult, *ibid.* **28**, 1698 (1995); M. Johansson, E. Malmström, A. Hult, *J. Polym. Sci. Polym. Chem. Ed.* **31**, 619 (1993).
5. S. R. Turner, B. I. Voit, T. H. Mourey, *Macromolecules* **26**, 4617 (1993).
6. D. H. Solomon, E. Rizzardo, P. Cacioli, U.S. Patent 4,581,429 (1986); M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, G. K. Hamer, *Macromolecules* **26**, 2987 (1993); C. J. Hawker, *J. Am. Chem. Soc.* **116**, 11185 (1994); D. Mardare and K. Matyjaszewski, *Macromolecules* **27**, 645 (1994); M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *ibid.* **28**, 1721 (1995).
7. Y. Ishihama, M. Sawamoto, T. Higashimura, *Polym. Bull.* **23**, 361 (1990); *ibid.* **24**, 201 (1990); *Macromolecules* **26**, 744 (1993).
8. C.-H. Lin, J. S. Xiang, K. Matyjaszewski, *Macromolecules* **26**, 2785 (1993).
9. G. A. Olah and S. J. Kuhn, U.S. Patent 3,024,291 (1962).
10. A typical polymerization procedure is done as follows. Tetrabutylammonium bromide [TBAB, 0.748 g (2.3×10^{-3} mol)] was placed in a reaction flask equipped with a three-way stopcock in a dry box. A solution of $SnCl_4$ (0.68 ml, 5.8×10^{-3} mol) in 3.9 ml of dry methylene chloride was added by dried syringe under continuous flow of dry N_2. The mixture was cooled to −20°C and a precooled solution of **1** (0.84 ml, 5.3×10^{-3} mol) in 5.2 ml of dry CH_2Cl_2 was added at once. After the addition, the reaction mixture turned transparently yellow, and its color changed to deep red during the polymerization. The polymerization system was quenched after 11 hours by addition of cold methanol (in excess to monomer). The reaction mixture was poured into 200 ml of CH_3OH to remove the remaining $SnCl_4$ and TBAB. The precipitate was filtered, dissolved in 50 ml of toluene, and washed three times with 2% aqueous solution of HCl and four times with distilled water. The organic layer was dried over $MgSO_4$ for several hours and concentrated. Toluene (10 ml) was then added and the solution was precipitated into 200 ml of CH_3OH. The polymer obtained was dried under dynamic vacuum at 50°C for 12 hours and subsequently analyzed by chromatographic and spectroscopic techniques. The polymers formed by this procedure are soluble in toluene, tetrahydrofuran, and chlorinated solvents.
11. Because tetrabutylammonium bromide was used in these reactions, the equilibria are more complex (Br^- ions are also involved). However, Matyjaszewski and co-workers (*8*) have pointed out that the $SnCl_4Br^-$ ions formed have a "similar effect on rates and polydispersities as [those produced from] tetrabutylammonium chloride" (p. 2790).
12. L. Rique-Lurbet, M. Schappacher, A. Deffieux, *Macromolecules* **27**, 6318 (1994).
13. It might be argued that possible heterogeneities in microstructure could affect data obtained across a single molecular weight distribution; therefore, our data were purposely taken with several samples, each of which yielded a data point representative of the entire sample.
14. Universal calibration is not always applicable to the characterization of M_r in dendritic polymers because of its heavy dependence on homogeneous density distribution throughout the whole macromolecule. It is used here to emphasize the differences in the solution behavior of the self-condensed vinyl polymers as compared with closely related, but linear, polymers.
15. I. Gitsov and J. M. J. Fréchet, *Macromolecules* **26**, 6536 (1993); *ibid.* **27**, 7309 (1994).
16. T. M. Chapman, G. L. Hillyer, E. J. Mahan, K. A. Shaffer, *J. Am. Chem. Soc.* **116**, 11195 (1994).

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Scanning Interferometric Apertureless Microscopy: Optical Imaging at 10 Angstrom Resolution

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Interferometric near-field optical microscopy achieving a resolution of 10 angstroms is demonstrated. The scattered electric field variation caused by a vibrating probe tip in close proximity to a sample surface is measured by encoding it as a modulation in the optical phase of one arm of an interferometer. Unlike in regular near-field optical microscopes, where the contrast results from a weak source (or aperture) dipole interacting with the polarizability of the sample, the present form of imaging relies on a fundamentally different contrast mechanism: sensing the dipole-dipole coupling of two externally driven dipoles (the tip and sample dipoles) as their spacing is modulated.

Near-field scanning microscopy at microwave frequencies (*1*) and its extension to the visible region [near-field scanning optical microscopy (NSOM)] (*2*, *3*) at resolutions under 50 nm have attracted much attention (*4–7*). Recently, a scanning interferometric apertureless microscope (SIAM) was introduced (*8*, *9*) with which one can measure the scattered electric-field variation caused by a vibrating and scanning probe tip in close proximity to a sample surface by encoding it as a modulation in the phase of one arm of an interferometer. Here, SIAM images of various samples are presented at a resolution of 1 nm, almost two orders of magnitude superior to that of other NSOM images. A basic theory based on coupled dipoles is put forward and compared with experiments. It shows that the contrast mechanisms are fundamentally different from those in regular near-field optical microscopes because of a unique dipole-dipole coupling mechanism. Furthermore, the theory predicts the ability to measure complex susceptibility down to the atomic level.

Experiments were performed in the transmission mode (*9*). An incident laser beam is focused on the back surface of a transparent substrate holding the sample (Fig. 1). A tip vibrating in the z direction (frequency f_z = 250 kHz, spring constant = 20 N/m, tip-end diameter ≃ 5 nm, vibra-

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