transitions and two melting points (Figure 4). These findings are fully consistent with our X-ray results, and together they demonstrate clearly the existence of molecular mixing between two polymers inside a crystal lattice.

As seen in Figures 2–4, specimens of blends crystallized at 120 °C have higher melting temperatures but lower Curie temperatures than their rapidly quenched counterparts. This is in exact agreement with the behavior found earlier by Green et al.[19] for *individual* copolymers. The dependence of the Curie transition on crystallization conditions is different between M1 and M2. In mixture M1, a single symmetric DSC peak appears for the sample that was crystallized at high temperature, i.e., above the Curie point, whereas an additional shoulder is seen after a rapid quench. On the other hand, in M2 a shoulder is seen when the sample had been crystallized above the Curie point, but not in the case of rapid quenching. In the latter case, the 65/35 mol % $VF_2/F_3E$ copolymer is known[20,21] to exhibit a double-Curie endotherm when crystallized at temperatures above ca. 100 °C; therefore, the appearance of the shoulder in curve D of Figure 3 is probably unrelated to the state of mixing of the two copolymers. In general, these various mixing effects are expected to depend upon the crystalline structures of the constituents, as well as upon kinetic factors. With respect to the first, we should note that crystallization at high temperatures occurs in the *paraelectric* phase, so that the ferroelectric lattice seen in the diffractograms of Figure 1 is adopted by the molecules only as a result of a solid-state transformation during cooling. Therefore, the difference in crystalline structures between the ferroelectric and paraelectric phases of both copolymers, as well as the associated differences in dipole–dipole interactions, will also play a role in the type and extent of mixing. These effects are being investigated.

In Figures 2–4 we also observe that the Curie temperature of mixture M1 is very close to that of the 52/48 mol % copolymer, and significantly sharper, whereas that of M2 is in the middle of the range between those of the individual constituents. The lattice spacing of M1 obtained by X-ray diffraction is located somewhat nearer to that of the 52/48 mol % copolymer, while that of M2 is very close to the spacing of the 65/35 mol % sample. These results are consistent with the expectation that the structure of the mixed crystals would be dictated primarily by the more disordered component.

The existence of two types of crystal in the M3 mixture (Figure 4) indicates a threshold in chemical and lattice differences with regard to cocrystallization. The slight decrease of the upper Curie temperature suggests that a small amount of the 52/48 mol % copolymer is contained in the crystals of the 73/27, thus introducing additional disorder. In this context, we found no compatibility in 50/50 wt % blends of these copolymers with *homopolymer* $PVF_2$ even in the melt.

In conclusion, our results from X-ray diffraction and DSC demonstrate cocrystallization within the same lattice by two polymers that possess similar chemical and crystalline structures. This similarity has to be close, as indicated by the formation of separate phases in blends of the 52/48 and 73/27 copolymers. Nevertheless, demonstration of such cocrystallization even among very similar macromolecules is remarkable, inasmuch as it has not been obtained in blends of other very similar polymers. For example, blends of ethylene/vinyl chloride copolymers studied over the full range of composition have been found[22] to be incompatible when one or both of the constituents is crystalline, even for compositions that differ by only a few percent. Even *deuteriated* polymers are generally incompatible with their protonated counterparts and form separate crystals (as, e.g., in polyethylene[23]).

We have also clearly demonstrated that solid-state transformations such as Curie transitions are very sensitive to the mixing state in crystals and therefore constitute potentially an ideal probe of cocrystallization in the same lattice. Modification of phase transitions, such as ferroelectric, ferromagnetic, or superconducting, induced by cocrystallization of two materials may be general in the condensed state.

A more detailed study of the compositional and temperature dependence of compatibility in our ferroelectric polymers, of their phase diagram, and of the dielectric and ferroelectric properties of their blends will be published elsewhere.

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**Registry No.** $(VF_2)(F_3E)$ (copolymer), 28960-88-5.

## References and Notes

(1) Permanent address: Department of Applied Physics, Faculty of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan.
(2) Nishi, T.; Wang, T. T. *Macromolecules* **1975**, *8*, 909.
(3) Tanaka, H.; Nishi, T. *Phys. Rev. Lett.* **1985**, *55*, 1102.
(4) Paul, D. R.; Newman, S. *Polymer Blends*; Academic: New York, 1978.
(5) Nishi, T. *CRC Crit. Rev. Solid State Mater. Sci.* **1985**, *12*, 329.
(6) Natta, G.; Allegra, G.; Bassi, I. W.; Sianesi, D.; Caporiccio, G.; Torti, E. *J. Polym. Sci. Part A* **1965**, *3*, 4263.
(7) Doll, W. W.; Lando, J. B. *J. Macromol. Sci., Phys.* **1970**, *B4*, 897.
(8) Guerra, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1986**, *19*, 1935.
(9) Starkweather, H. W., Jr. *J. Appl. Polym. Sci.* **1980**, *25*, 139.
(10) Martynowicz-Hans, L. M.; Runt, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27*, 269.
(11) Harris, J. E.; Robinson, L. M. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 311.
(12) Aubin, M.; Bedard, Y.; Morrissette, M. F.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 233.
(13) Neira-Lemos, R. A. Ph.D. Thesis, University of Massachusetts, 1974.
(14) Roerdink, E.; Challa, G. *Polymer* **1978**, *19*, 173.
(15) Bosscher, F.; Brinke, G. T.; Challa, G. *Macromolecules* **1982**, *15*, 1442.
(16) Tashiro, K.; Takano, K.; Kobayashi, M.; Chatani, Y.; Tadokoro, H. *Ferroelectrics* **1984**, *57*, 297.
(17) Lovinger, A. J.; Furukawa, T.; Davis, G. T.; Broadhurst, M. G. *Ferroelectrics* **1983**, *50*, 227; *Polymer* **1983**, *24*, 1225, 1233.
(18) Davis, G. T.; DeReggi, A. S.; Chen, D. Y. presented at the Meeting of the American Physical Society, New York, March 1987; paper AV3.
(19) Green, J. S.; Farmer, B. L.; Rabolt, J. F. *J. Appl. Phys.* **1986**, *60*, 2690.
(20) Tanaka, H.; Yukawa, H.; Nishi, T., unpublished results.
(21) Davis, G. T.; Broadhurst, M. G.; Lovinger, A. J.; Furukawa, T. *Ferroelectrics* **1984**, *57*, 73.
(22) Bowmer, T. N.; Tonelli, A. E. *Macromolecules* **1986**, *19*, 498.
(23) Schelten, J.; Wignall, G. D.; Ballard, D. G. H.; Longman, G. W. *Polymer* **1977**, *18*, 1111.

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## Low Polydispersity Homopolymers and Block Copolymers by Ring Opening of 5,6-Dicarbomethoxynorbornene

In general, classical metathesis catalysts will not tolerate functionalities such as the carbonyl group.[1] In some cases

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**Table I**
**Polymers Prepared from Norbornene and *endo,endo*-5,6-Dicarbomethoxynorbornene**[a]

| equiv of monomer | $M_n$ (theory) | $M_n$ (found) | polydispersity |
|---|---|---|---|
| 50 NBE | 4870 | 13500 | 1.11 |
| 100 NBE | 9580 | 22100 | 1.06 |
| 200 NBE | 19000 | 48600 | 1.04 |
| 100 NBE | 9580 | 21900 | 1.07[b] |
| 50 DCNBE | 10700 | 17400 | 1.11 |
| 100 DCNBE | 21200 | 37700 | 1.12 |
| 200 DCNBE | 42200 | 63300 | 1.22 |
| 50 + 200[c] | 29500 | 59900 | 1.09 |
| 200 + 50[d] | 29500 | 57200 | 1.06 |

[a] All reactions were performed in the same manner.[5] Molecular weights are relative to polystyrene; approximate true molecular weights can be obtained by dividing by 2.2.[1a,3] [b] Reaction performed in the presence of 10 equiv of ethyl acetate. [c] 50 equiv of *endo,endo*-5,6-dicarbomethoxynorbornene followed by 200 equiv of norbornene. [d] 200 equiv of norbornene followed by 50 equiv of *endo,endo*-5,6-dicarbomethoxynorbornene.

it has proven possible to ring-open polymerize functionalized norbornenes, although it has never been shown that none of a given catalyst is destroyed during the course of the reaction.[1d] Recently we have shown that catalysts of the generic type W(CHR′)(NAr)(OR)$_2$ (Ar = 2,6-diisopropylphenyl; R and R′ = alkyl groups[2]) will react with norbornene when OR = *tert*-butoxide to give polynorbornene with a polydispersity approaching 1[3] and that analogous molybdenum complexes of the type Mo(CHR′)(NAr)(OR)$_2$ are active for the metathesis of ordinary olefins at rates that vary from very fast when OR = OCMe(CF$_3$)$_2$ to virtually zero when OR = *tert*-butoxide.[4] We have found that W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ will polymerize *endo,endo*-5,6-dicarbomethoxynorbornene, but the catalyst is destroyed rapidly and molecular weight therefore cannot be controlled. We suspected that the metal–carbon bond in Mo(CHR)(NAr)(O-*t*-Bu)$_2$ might not be as strongly polarized as it is in W(CHR)(NAr)(O-*t*-Bu)$_2$ and therefore that molybdenum complexes would not react as readily with the ester functionality as tungsten complexes. We show here that Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ is an initiator in a living polymerization reaction in which at least 100 equiv of the ester carbonyl (50 equiv of monomer) is tolerated on the time scale of a typical polymerization (~15 min).

The addition of norbornene to a solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$[4] (**1**) under standard reaction conditions[5] yielded low dispersity polynorbornenes with molecular weights proportional to the quantity of monomer employed (Table I, entries 1–3). If only 10 equiv of norbornene is added to an NMR sample of **1** in C$_6$D$_6$ (H$_\alpha$ at 11.23 ppm) a new alkylidene H$_\alpha$ signal can be observed at 11.52 ppm, a doublet characteristic of Mo[[CH(C$_5$H$_8$)CH]$_x$*CH*-*t*-Bu](NAr)(O-*t*-Bu)$_2$ (**2**) (cf. H$_\alpha$ at 8.05 ppm in W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and 8.36 ppm in W[[CH(C$_5$H$_8$)CH]$_x$CH-*t*-Bu](NAr)(O-*t*-Bu)$_2$[3]); the ratio of **1** to **2** is 1:9, and the total is equal to the initial amount of **1** (versus an internal standard). If only 1 equiv of norbornene is employed then 83% **1** remains. These results suggest that the rate of initiation by **1** is slightly slower than the rate of propagation by **2**,[6] presumably for steric reasons. All polynorbornene obtained by employing **1** at 25 °C is ~55% trans. A sealed NMR sample that had been prepared with 20 equiv of norbornene (91/9 ratio of **2** to **1**; 54% trans) changed little in 2 weeks (93:7 ratio of **2** to **1**; 57% trans), signifying that the living polymer does not isomerize C=C bonds in the polymer chain. (Isomerization of cis to trans (~85%) in such polymers is observed if catalysts that are active for metathesis of ordinary olefins, e.g., Mo(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$,[4] are added; **1** is virtually inactive for the metathesis of *cis*-2-pentene.)

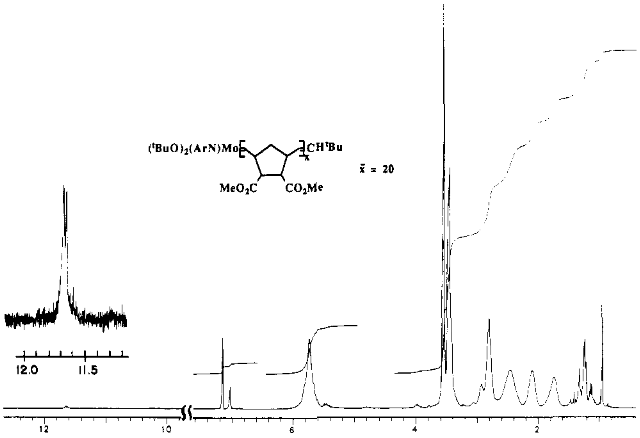

**Figure 1.** $^1$H NMR spectrum of a sample of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ after addition of 20 equiv of *endo,endo*-5,6-dicarbomethoxynorbornene.

We first showed that norbornene could be polymerized in the presence of 10 equiv of ethyl acetate. Entry 4 in Table I shows that polynorbornene prepared from 100 equiv of NBE is virtually identical with that obtained in the absence of ethyl acetate, good evidence that the Mo=C bonds are not destroyed to any significant extent by 10 equiv of the ester during the polymerization reaction (10–15 min).

Addition of 20 equiv of *endo,endo*-5,6-dicarbomethoxynorbornene (DCNBE) to **1** in C$_6$D$_6$ quantitatively converted it (versus an internal standard) into a living polymer (**3**; Figure 1) that has an alkylidene H$_\alpha$ signal at 11.64 ppm. The olefinic proton resonances in what we presume to be a mixture of cis and trans polymer at 5.75 ppm could not be resolved. If only 1 equiv of DCNBE is added to **1**, 68% **1** remains. Therefore we can say that **1** is converted more efficiently to the living polymer in the case of DCNBE than in the case of NBE, although initiation is the slower step in both cases.[6,8] When 50 and 100 equiv of DCNBE are added to **1** in a manner analogous to the reactions in which polynorbornene is prepared, the resulting polymer has a low polydispersity, characteristic of a living polymerization catalyst system (Table I). The fact that the polydispersity with 100 equiv is not quite as good as that for the analogous polynorbornene suggests that there may be some slow destructive reaction between the catalyst and the ester carbonyl group. This is supported by the fact that the polymer prepared by using 200 equiv of DCNBE, although it has the expected molecular weight relative to the polymer prepared by employing 100 equiv of DCNBE, has an even higher polydispersity. Poly-DCNBE is much less viscous that polynorbornene, and systems in which it is prepared therefore are more easily manipulated. Full characterization of it and related polymers will be reported in due course.

If a living polymer containing 20 equiv of NBE is prepared and 20 equiv of DCNBE is added to it, an $^1$H NMR spectrum shows that the H$_\alpha$ resonance for **2** is completely replaced by one characteristic of **3** and that the remainder of the spectrum is a virtual composite of that for **2** and that for **3** (Figure 2). An analogous sample prepared by adding 20 equiv of DCNBE first, followed by 20 equiv of NBE, has an identical spectrum, except the chemical shift of the H$_\alpha$ resonance is close to that of **2**. The carbon NMR spectra of the **2**/**3** and **3**/**2** block copolymers also are virtual composites of the spectra for the individual homopolymers when the chain is relatively long (>20 units).

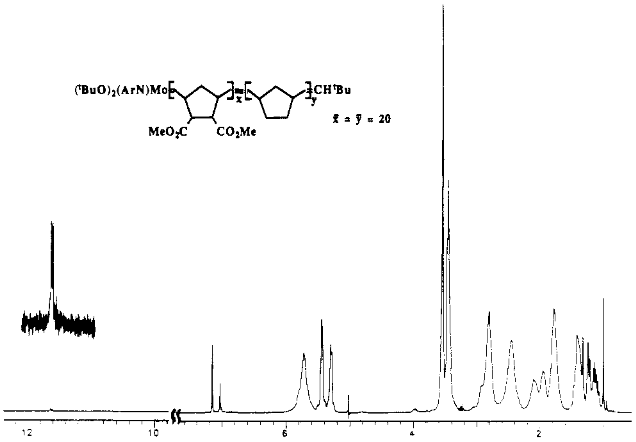

**Figure 2.** $^1$H NMR spectrum of a sample of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ after addition of 20 equiv of norbornene followed by 20 equiv of *endo,endo*-5,6-dicarbomethoxynorbornene.

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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## References and Notes

(1) (a) Ivin, K. J. *Olefin Metathesis*; Academic: London, 1983. (b) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Elmsford, NY, 1982; Vol 8. (c) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring-opening Polymerization of Cyclo-Olefins*, 2nd ed.; Wiley-Interscience: New York, 1985. (d) It has been stated (ref 1a, p 260) that *exo,-endo*-5,6-dicarbomethoxynorbornene has been polymerized. To our knowledge this was not a controlled polymerization analogous to that we report here for the endo,endo monomer. Polymerization of the endo,endo monomer has never been reported.

(2) Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771.

(3) Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1169.

(4) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373.

(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.

(7) Peebles, L. H., Jr. *Molecular Weight Distributions in Polymers*; Wiley-Interscience: New York, 1971.

(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 $\xi$. 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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