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(18) IR spectra of the polymers present only ester carbonyl absorptions at 1748 and 1775 cm^{-1}, whereas peaks attributed to unreacted COOH are not present.
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Ring Strain Is Not an Important Factor Contributing to the Rate of Olefin Metathesis Polymerization

It has been widely asserted that the rate of polymerization of cyclic olefins by metathesis catalysis is a function of ring strain in the monomer.[1-3] Strained olefins such as cyclobutene and norbornene have been used to test sluggish catalysts for activity.[4] This communication questions these assertions and offers another interpretation of the kinetic data, namely that reactivity differences between different cyclic olefins can be attributed to the relative reactivity of the propagating carbenes. The geometry of the growing polymer chain about the catalyst site determines the reactivity.

Whether ring strain should increase or decrease the rate of metathesis polymerization is, a priori, not obvious. Scheme I depicts the generally accepted mechanism for the propagation step in cyclic olefin metathesis polymerization. Whether the coordination step is association–dissociation or dissociation–association, whether or not the penultimate or other chain double bond is coordinated, and whether or not a cocatalyst is involved are not considered and are extraneous to this argument. If k_1 or k_3 is the overall rate-determining step, a strained cyclic olefin could be expected to react faster than one with less strain: the coordination of a strained olefin or the opening of fused strained rings would lower the free energy of the transition state. If, however, k_2 is rate limiting, ring strain could impede the reaction: formation of fused strained rings would raise the free energy of the transition state. It has been pointed out[3] that differences in energy between **1**, **2**, and **3** must be small to explain the observed rates and activation parameters. Experiments detailed below suggest that ring strain in the cyclic olefin does little to affect the polymerization rate and that the rate is principally a function of the structure of **1**.

Figure 1 displays first-order plots for three polymerization reactions: norbornene (NBE) and cyclooctene (COE) homopolymerizations and a COE polymerization to which 0.34 equiv of NBE was added at t = 10 min (90% of the COE was unreacted at this point). Tungsten hexachloride/tetramethyltin was the catalyst; the solvent was chlorobenzene. The initial monomer/catalyst ratio was 11/1/1 COE/W/Sn and the initial monomer concentration was 0.37 M. NBE homopolymerizes at an unmeasurably large rate under these conditions and has the effect of increasing the rate of COE polymerization: upon NBE addition (at 10 min) the rate of COE consumption increases by ~6-fold and after the NBE is depleted, the rate returns to its initial value. Accurate rate constants cannot be determined from the plots in Figure 1, but qualitatively we can say that NBE homopolymerizes >100 times as fast as COE (separate polymerizations), but in a competitive experiment (NBE and COE in same polymerization) NBE reacts only 2–3 times as fast as COE.

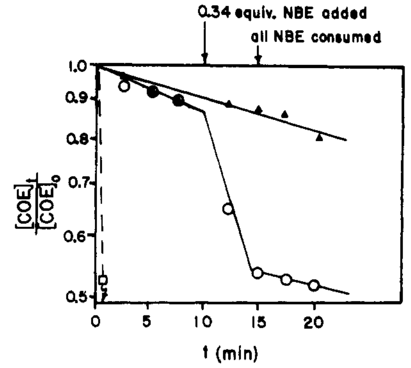
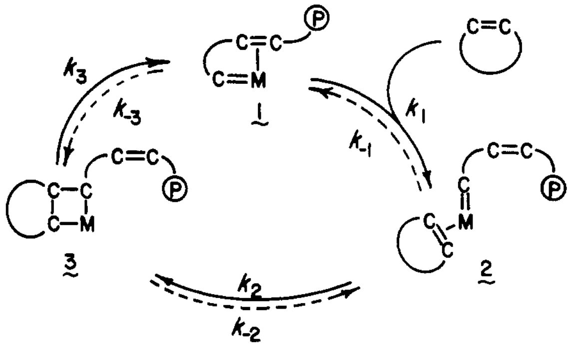
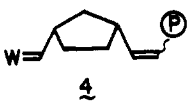


Figure 1. Homopolymerizations of NBE (□) and COE (△) and polymerization of COE to which 0.34 equiv of NBE was added at t = 10 min (○). $[NBE]_0$(homopolymerization) = 0.13 M, $[COE]_0$ = 0.37 M, T = 25 °C.

Scheme I
Propagation Step in Cyclic Olefin Metathesis Polymerization



We interpret this result in terms of the relative reactivity of NBE- and COE-derived carbenes (**4** and **5**, respectively).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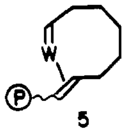
5

The olefin in **4** cannot coordinate with the carbene tungsten as in **5**, making **4** the more reactive carbene. When present with both COE and NBE, **4** is not very selective, and COE competes effectively. Ring strain in NBE, therefore, cannot be the reason for its greater (than COE) reactivity.

The same type of experiments have been performed with NBE and 1,5-cyclooctadiene (COD). Similar results were obtained (Figure 2) and we interpret them identically.

In an attempt to determine the relative stabilities of COE-derived carbene **5** and COD-derived carbene **6**, the experiments detailed in Figure 3 were performed. In

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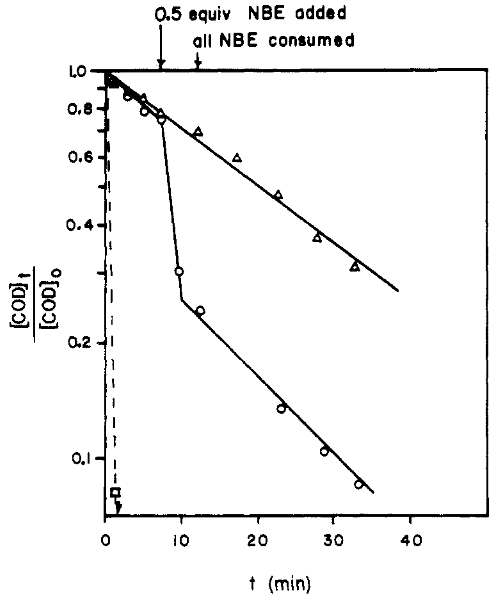


Figure 2. Homopolymerizations of NBE (□) and COD (△) and polymerization of COD to which 0.5 equiv of NBE was added at t = 10 min (○). $[NBE]_0$(homopolymerization) = 0.17 M, $[COD]_0$ = 0.35 M, T = 35 °C.

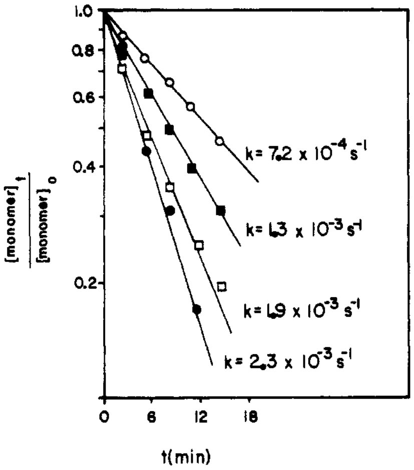
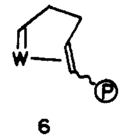


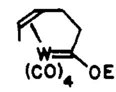
Figure 3. Homopolymerizations of COE (□) and COD (○) and copolymerization of COE (■) and COD (●): $[monomer]_0$ = 0.4 M, T = 80 °C.

side-by-side homopolymerizations, COE reacts 2.7 times as fast as COD, but in a copolymerization the relative reactivity switches: COD then reacts 1.8 times as fast as COE, presumably because it contains two double bonds. We conclude that 5 is more reactive than 6. That 6 should



6

be a particularly unreactive olefin–carbene complex is shown by the fact that 7 has recently been isolated and its structure determined.[5,6] These authors also point out that 8 is less stable than 7.



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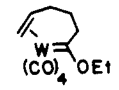

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Surface Modification of Poly(tetrafluoroethylene) with Benzoin Dianion

Poly(tetrafluoroethylene) (PTFE) is a highly chemically resistant polymer, inert to a wide variety of reagents.[1,2] In contrast to its behavior with most chemicals, PTFE reacts readily with strong reducing agents,[3-11] particularly alkali metals, to produce black-colored materials which have been described as carbonaceous,[3,4] containing carbon and oxygen in a ratio of ~1:0.3,[5,6] containing carbon radicals and carbon–carbon double bonds,[5] amorphous carbon interspersed with alkali metal fluoride,[7] intercalated carbon,[8] polymeric carbon and alkali fluoride,[9] polymeric anion radicals,[10] and alkali fluoride doped poly(fluoroacetylene).[11] In this communication we report a new and significantly different reduction of PTFE which does not involve alkali metals as the reducing agent. The reduced polymer is likewise different from the alkali-reduced materials: the surface exhibits a reflective metallic lustre instead of the black color which is characteristic of reduced Teflon.

Experimental Section. Virgin PTFE film (Commercial Plastics/Du Pont Teflon) (5 mils) was extracted with tetrahydrofuran for 24 h in a Soxhlet extractor and dried under vacuum at 60 °C to constant weight. Benzoin was purchased from Aldrich and recrystallized twice from ethanol to a constant melting point of 96 °C and stored in a vacuum desiccator. Potassium *tert*-butoxide was purchased from Aldrich and used without further purification. Doubly distilled water (Gilmont still) was degassed by purging with nitrogen; THF was distilled from sodium benzophenone dianion; Me_2SO was distilled from CaH_2 at reduced pressure.

Gravimetric analyses were performed with a Cahn 29 electrobalance. Scanning electron micrographs of gold sputter-coated samples were obtained with a JEOL 100 CX. ESCA spectra were recorded using a Mg Kα source with a Kratos XSAM 800 spectrometer. UV–vis spectra were obtained directly from films using a Perkin-Elmer 100A with a virgin PTFE sample in the reference beam.

Reduction. Potassium *tert*-butoxide (4.0 g, 35 mmol) was dissolved in 35 mL of Me_2SO and added to a 5-mL Me_2SO solution of 0.27 g (1.3 mmol) of benzoin under nitrogen. A dark purple color (indicative of the radical anion of benzoin) forms, and this solution is transferred