HMDB (1) is raised in the sample. A propensity for ion–molecule reactions of this kind in the relatively mobile $CF_2ClCFCl_2$ matrix has been amply documented.[5] The closing argument is that the six-line spectrum can be assigned to radical 3. This is straightforward since the average ^1H hfs of 14.4 G is typical of α- and β-hydrogen splittings for allylic radicals[5a,8] and coupling to five nearly equivalent hydrogens (H^α_{exo}, H^α_{endo}, and $3H^\beta_{endo}$) is predicted in this case.[8a]

We conclude that there is no credible evidence for the formation of the $^2A_1$ state of the HMDB radical cation in $CF_2ClCFCl_2$,[1] the $^2B_2$ state being produced as in $CFCl_3$.[2] The different results obtained previously in these two matrices[1,2] originate from the greater proclivity for loss of the $^2B_2$ radical cation by ion–molecule reactions in the more mobile $CF_2ClCFCl_2$ solid, especially at high HMDB concentrations. Consequently, the $^2B_2$ and not the $^2A_1$ radical cation[1] is the ground state in these Freon matrices.[9,10] Trifunac and co-workers have similarly observed only the $^2B_2$ state from measurements of time-resolved fluorescence detected magnetic resonance in liquid cyclopentane and n-pentane solutions,[11] and so there is no evidence for a solvent effect on the nature of the ground state as was suggested earlier.[12]

Registry No. 1, 7641-77-2; 2, 85293-78-3; 3, 75650-90-7.

(8) Berndt, A. In *Landolt-Börnstein*; New Series, Group 11, *Magnetic Properties of Free Radicals*; Fischer, H., Hellwege, K.-H., Eds.; Springer-Verlag: Berlin-Heidelberg, 1977; Vol. 9, Part b, pp 345–353. Berndt, A. In *Landolt-Börnstein*; New Series, Group II, *Magnetic Properties of Free Radicals*; Fischer, H., Ed.; Springer-Verlag: Berlin-Heidelberg, 1987; Vol. 17 (Supplement and Extension to Vol. 9), Subvolume c, pp 8–12 and 48–54.

(9) This conclusion rests on two counts. First, only the $^2B_2$ state of the HMDB radical cation is detected initially at 80 K; also, its signal intensity remained unchanged on thermal cycling to higher temperatures, thereby providing no evidence for a process of thermal equilibration to a lower lying state. Thus, in experiments with *dilute* HMDB solutions in both $CF_2ClCFCl_2$ and $CFCl_2CFCl_2$, the $^2B_2$ state persisted from 80 to 100 K before undergoing the ring-opening rearrangement as in the CFCl$_3$ matrix.[2] Indeed, this *unimolecular* reactivity of the $^2B_2$ radical cation was found to be very similar in all three matrices, as expected for thermalized species.[9a] Secondly, the complementary relationship between the $^2B_2$ state and the allylic radical as a function of HMDB concentration in $CF_2ClCFCl_2$ clearly argues in favor of a single HMDB radical cation undergoing the bimolecular reaction in Scheme I. In sum, the evidence is overwhelming that the $^2B_2$ species is the ground state of the HMDB radical cation in these matrices. Finally, we note that the $^2A_1$ species could well be a metastable precursor to the hexamethylbenzene radical cation formed from the $^2B_2$ state on annealing although there is no direct evidence for its involvement in this reaction. A similar situation applies to the ring opening of the bicyclo[2.2.0]hexane radical cation.[4b] (a) The matrix dependence of unimolecular radical cation rearrangements mentioned in the opening paragraph refers to nonthermal activation processes that sometimes occur in the course of radical cation generation.[4] In this case, *the initial distribution* of reactant and product radical cations depends on the matrix, a good example being the very different ratios of the cyclohexane-1,4-diyl and cyclohexene radical cations produced from the radiolytic oxidation of 1,5-hexadiene in CF$_3$CCl$_3$ and CFCl$_3$.[4a]

(10) Rhodes claimed that his assignment of the apparent seven-line spectrum to the $^2A_1$ state was strongly supported by the appearance of features from the ring-opened hexamethylbenzene radical cation on annealing of the sample.[1] These features were relatively weak, however, and can now obviously be attributed to the ring opening of residual $^2B_2$ radical cations.[9]

(11) Qin, X.-Z.; Werst, D. W.; Trifunac, A. D. *J. Am. Chem. Soc.*, first of three papers in this issue.

(12) See footnote 5 of ref 1.

(13) (a) An independent ESR and ENDOR study has also assigned the six-line spectrum to radical 3: Arnold, A.; Gerson, F. *J. Am. Chem. Soc.* **1990,** *112,* 2027.

rac-[Ethylidene(1-η^5-tetramethylcyclopentadienyl)(1-η^5-indenyl)]dichlorotitanium and Its Homopolymerization of Propylene to Crystalline–Amorphous Block Thermoplastic Elastomers

Daniel T. Mallin,[1a] Marvin D. Rausch,*,[1a] Ye-Gang Lin,[1b] Sizhong Dong,[1c] and James C. W. Chien*,[1c]

Departments of Chemistry, Chemical Engineering, and Polymer Science and Engineering
University of Massachusetts
Amherst, Massachusetts 01003
Received October 23, 1989

ansa-Metallocene compounds have been discovered that polymerize propylene with either isospecificity[2,3] or syndiospecificity[4] to predominantly isotactic or syndiotactic polymers, respectively. In this contribution, we describe the formation of a new *ansa*-metallocene system, *rac*-[ethylidene(1-η^5-tetramethylcyclopentadienyl)(1-η^5-indenyl)]dichlorotitanium (1), which produces homopolypropylene having the attributes of a thermoplastic elastomeric (TPE) material.

A reaction[5] between 1,2,3,4,6-pentamethylfulvene[6] and indenyllithium in THF solution, followed by hydrolysis and distillation, afforded 1-(1-indenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)-ethane (2) (bp 130–140 °C/0.1 Torr) in 54% yield [anal. (calcd): C, 90.63 (90.85); H, 9.25 (9.15)]. The golden orange oil 2 is an isomeric mixture according to ^1H and ^{13}C NMR. A solution of 2 (13 mmol) in 150 mL of THF was cooled to 0 °C, n-butyllithium (26 mmol) was added dropwise, and the mixture was stirred for several hours at 40 °C to from a deep red solution. It was cooled to –78 °C, and 13 mmol of $TiCl_4(THF)_2$[7] in THF was added dropwise. Subsequent refluxing for 18 h gave a green solution. Removal of the solvent, extraction with CH_2Cl_2, filtration, and removal of the CH_2Cl_2 gave 4.7 g of 1 in 95% crude yield. The product was purified by crystallization from CH_2Cl_2/n-hexane, MS m/e 381 for M$^+$; [anal. (calcd): C, 61.41 (63.02); H, 5.70 (5.82)]. The ^1H and ^{13}C NMR[8] spectra indicate that only one of the two possible diasteromeric pairs is isolated, with the probable structure shown based on steric considerations.

1
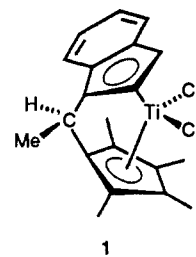
Polymerization of propylene[9] at 1.5 atm and 50 °C with 27 μM 1 and 54 mM methylaluminoxane (MAO)[3,9] based on Al for 1

(1) (a) Department of Chemistry. (b) Department of Chemical Engineering. (c) Department of Polymer Science and Engineering.

(2) (a) Ewen, J. A. *J. Am. Chem. Soc.* **1984,** *106,* 6355. (b) Ewen, J. A. Ligand Effects on Metallocene Catalyzed Polymerizations. In *Catalytic Polymerization of Olefins*; Keii, T., Soga, K., Eds.; Elsevier: New York, 1986; p 271. (c) Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987,** *109,* 6544.

(3) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985,** *24,* 507.

(4) Ewen, J. A.; Jones, R. L.; Razavi, A. *J. Am. Chem. Soc.* **1988,** *110,* 6255.

(5) The addition reaction of organometallic compounds to fulvenes was first described by Ziegler and Schäfer: Ziegler, K.; Schäfer, W. *Justus Liebigs Ann. Chem.* **1934,** *511,* 101.

(6) (a) Bensley, D. M., Jr.; Mintz, E. A. *J. Organomet. Chem.* **1988,** *353,* 93. (b) Mallin, D. T.; Rausch, M. D.; Mintz, E. A.; Rheingold, A. L. *J. Organomet. Chem.,* in press.

(7) Manzer, L. E. *Inorg. Synth.* **1982,** *21,* 135.

(8) ^1H NMR: (200 MHz) 1.68 (s, 3 H), 1.95 (s, 3 H), 1.96 (s, 3 H), 1.98 (s, 3 H), 2.19 (d, 3 H, *J* = 7.5 Hz), 4.96 (q, 1 H), 5.70 (d, 1 H), 6.95–7.59 (m, 5 H). ^{13}C NMR: (200 MHz) 12.7, 12.8, 14.9, 16.1, 18.4, 30.3, 93.3, 96.8, 112.6, 121.7, 123.4, 124.4, 125.2, 126.3, 126.6, 128.1, 130.0, 133.3, 136.9, 137.9.

(9) Chien, J. C. W.; Wang, B. P. *J. Polym. Sci., Polym. Chem. Ed.* **1988,** *26,* 3089.

Table I. Mechanical and Thermal Properties of TPE Polypropylenes

sample	3	4
strength, MPa	3.97	12.1
strain to break, %	525	1260
recovery after break, %	86	94
G_{eq}, MPa	1.47	0.56
T_m,[a] °C	51.2, 66.0	53.1, 63.8
ΔH_f,[a] cal g^{-1}	3.26	2.93

[a] Samples annealed at 30 °C for 12 h before DSC scan.

Table II. Elastomeric Properties of TPE Polypropylenes

sample	3			4		
strain, %	100	200	300	100	200	300
stress, MPa	3.13	3.39	3.53	3.07	3.30	3.59
recovery, %	93	91	83	97	96	92

h gave 0.74 g of polypropylene (PP) 3, which corresponds to a catalytic activity of 2.5 × 10⁵ g of PP (mol of Ti)$^{-1}$ h^{-1} atm^{-1}. Polymerization at 25 °C also yielded polypropylene 4. Polymers 3 and 4 were subjected to solvent fractionation.[10] Aside from a very small amount of acetone-soluble material, the polymers are completely soluble in refluxing ethyl ether, indicating uniformity of structure. They are also characterized by narrow molecular weight distributions. According to GPC using columns calibrated with polypropylenes of known $\bar{M}_w$, 3 has $\bar{M}_n$ = 66 600, $\bar{M}_w$ = 127 000, and $\bar{M}_w/\bar{M}_n$ = 1.9 and 4 has $\bar{M}_n$ = 98 400, $\bar{M}_w$ = 164 000, and $\bar{M}_w/\bar{M}_n$ = 1.7. The degree of crystallinity was found by Roland analysis of X-ray powder patterns obtained on samples annealed between 30 and 45 °C to be 28.6 ± 0.5% and 26.5 ± 0.4% for 3 and 4, respectively. The polymers exhibit more than one melting endotherm; the transition temperature (T_m) and enthalpy (ΔH_f) obtained by DSC on samples annealed at 30 °C for 12 h are given in Table I. Annealing at lower temperatures resulted in lower T_m, which indicates a dependence of the size and order of crystalline domains on crystalline conditions.

The dynamic storage modulus (G') measured at 1 rad s^{-1} as a function of temperature showed a 3 orders of magnitude decrease between 60 and 80 °C due to the melting transition. G' increases only slightly with frequency at 50 °C but increases strongly with frequency at 100 °C, indicating an elastomeric state in the former but a single phase melt state in the latter. Stress–strain curves obtained on dogbone samples (molded at 100 °C, annealed at 60 °C for 2 h) showed very strong mechanical properties (Table I). In particular, 4 did not break until stretched beyond 1260%. The polymers exhibit excellent elastic recoveries (Table II); the strain recovery is better than 90% for 4 after elongation of 100–300%. These properties can be explained only by the presence of physical cross-links due to crystallization of stereoregular segments of the polypropylene chains. The molecular weight between cross-links ($\bar{M}_c$) was estimated from the equilibrium modulus (G_{eq}), which was measured at 50 °C, 0.5% strain, and stress relaxed for 10⁴ s (Table I). The estimates for $\bar{M}_c$ [=(density)RT/G_{eq}] are 2.0 × 10³ and 4.4 × 10³ for 3 and 4, respectively. Since the crystallizable segments in the polymer chains must be quite short as indicated by the low T_m, there are many alternating crystallizable and noncrystallizable segments, of the order of 20.[11] These polymers contain low homosteric pentad populations.[12] The detailed analysis of 500-MHz ¹³C NMR spectra will be reported elsewhere.

Ewen pointed out that for syndiospecific propylene polymerization using (isopropylidenecyclopentadienyl-1-fluorenyl)dichlorohafnium, there is chain migration following each monomer insertion.[4] The bridging carbon in 1 is chiral and can have the polymer chain either syn (1a) or anti (1b) to the ansa-methyl group during polymerization.

1a   1b
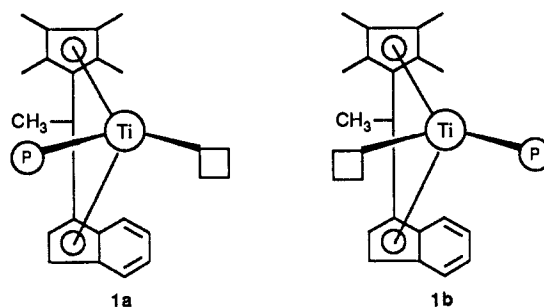
The block structure of the present TPE polypropylene may be explained by postulating that during chain propagation on 1a or 1b they undergo occasional interconversion,

$$\text{stereoregular segment} \xleftarrow{k_{pi}} \mathbf{1b} \underset{k_{bi}}{\overset{k_{ab}}{\rightleftharpoons}} \mathbf{1a} \xrightarrow{k_{pa}}$$

amorphous segment
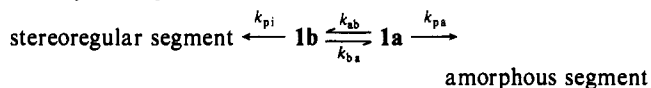
where the k_p's are greater than k_{ab} and k_{ba}. The resulting polymer is microphase separated into crystalline and amorphous domains, and the former act as physical cross-links. Above T_m, the polymers are linear viscoelastic.

The above results demonstrate that 1 can produce polypropylene chains containing alternating crystallizable and noncrystallizable segments in any given chain. The polymers are quite homogeneous in structure as well as molecular weight. This is the first example of a thermoplastic elastomer comprising a single monomer.[13,14]

(13) Polypropylenes exhibiting elastomeric properties have been obtained by Tullock and co-workers[14] using alumina-supported bis(arene) Ti, Zr, and Hf catalysts. Their materials contain chains soluble in ethyl ether, hexane, heptane, and octane, as well as octane-insoluble ones. Hysteresis curves showed 110% permanent set after 300% elongation.

(14) (a) Tullock, C. W.; Tebbe, F. N.; Mulhaupt, R.; Overall, D. W.; Selterquist, R. A.; Ittel, S. D. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 3063. (b) Collette, J. C.; Tullock, C. W.; MacDonald, R. N.; Buck, W. H.; Su, A. C. L.; Harrell, J. R.; Mulhaupt, R.; Anderson, B. C. *Macromolecules* **1989**, *22*, 2851.

(10) Pasquon, I. *Pure Appl. Chem.* **1967**, *15*, 465.

(11) This *crude* estimate assumes that the crystallizable segments comprise about 20 monomer units. It is dependent upon the crystallization conditions.

(12) The average steric pentad distributions for 3 by the methyl ¹³C NMR spectrum are as follows: [mmmm] = 0.40, [mmmr] = 0.16, [rmmr] = 0.043, [mmrr] = 0.15, [mrmm] + [rmrr] = 0.07, [rmrm] = 0.034, [rrrr] = 0.02, [rrrm] = 0.043, and [mrrm] = 0.07.

Oxygen Atom Transfer from O₂ to a Coordinated Olefin: A New Route to Oxametallacyclobutanes

V. W. Day,[*,1a] W. G. Klemperer,[*,1b] S. P. Lockledge,[1b] and D. J. Main[1b]

Department of Chemistry, University of Nebraska Lincoln, Nebraska 68588
Crystalytics Company, Lincoln, Nebraska 68501
Department of Chemistry, University of Illinois Urbana, Illinois 61801

The selective oxidation of ethylene to ethylene oxide over Ag/Al₂O₃ is a process having major industrial importance due to its efficiency and simplicity.[2] Little is known about the detailed mechanism of O₂ to ethylene oxygen atom transfer in this system, however, except that ethylene reacts with adsorbed atomic oxygen as opposed to adsorbed molecular oxygen.[2] Given the fundamental significance of this process and oxygen activation processes in general,[3] we have synthesized a series of polyoxoanion-supported

(1) (a) Crystalytics Company. (b) University of Illinois.
(2) (a) Van Santen, R. A.; Kuipers, H. P. C. E. *Adv. Catal.* **1987**, *35*, 265. (b) Roberts, J. T.; Madix, R. J. *J. Am. Chem. Soc.* **1988**, *110*, 8540.