Mechanism of Trialkylborane Promoted Adhesion to Low Surface Energy Plastics

Mark F. Sonnenschein,* Steven P. Webb, Patrick E. Kastl, Daniel J. Arriola, Benjamin L. Wendt, and Daniel R. Harrington

Dow Chemical Company, Corporate Research and Development, Midland, Michigan 48674

Nelson G. Rondan

Dow Chemical Co., Corporate Research and Development, Freeport, Texas 77541

Received May 27, 2004; Revised Manuscript Received July 23, 2004

ABSTRACT: Excellent adhesion to low surface energy substrates such as polypropylene, polyethylene, poly(vinyl difluoride), and poly(tetrafluoroethylene) is obtained with acrylic polymerization initiated by trialkylboranes at room temperature and without need for surface pretreatment. The mechanism of adhesion is a consequence of a series of radical processes resulting from the initial oxidation of the trialkylborane followed by the production of alkoxy and alkyl radicals. This paper will elucidate the mechanism of adhesion using both experiment and theory.

Introduction

Polyolefins such as polyethylene, polypropylene, and their copolymers are useful in the fabrication of many objects including automotive components, footwear, toys, and household appliances. These polymers are inexpensive and lightweight and can be tailored to achieve a wide range of properties. Unfortunately, the inherent low surface energy of polyolefins inhibits adhesion to most adhesive and coating formulations[1] which tend to contain polar materials such as urethanes, acrylics, and epoxies.[2] Consequently, efforts have been directed toward pretreating the surface of these low surface energy materials in order to achieve satisfactory adhesion. Such pretreatments include vapor cleaning, acid treating, priming, corona discharge treating, or plasma treating.[3−11] Other efforts to improve adhesion have been directed to the use of adhesion promoters.[12] Unfortunately, such techniques are often cumbersome, costly, and environmentally unsound. Recently, we[13] and others[14−17] have disclosed new technology that provides very strong adhesion to polyolefins and fluorinated polymers at room temperature and without the need for surface pretreatment. Adhesion to these plastic substrates is promoted by trialkylborane catalysts that produce radical initiators at room temperature. Previous work had speculated that trialkylboranes produced radical initiators through an SN1 insertion of oxygen to the empty p orbital of boron with the concomitant production of an alkyl radical and peroxy radical. However, these radicals are usually insufficiently energetic for the kind of chemistry that might result in adhesion to olefin substrates. In this article we provide evidence supporting a proposed mechanism involving insertion of oxygen between the boron and an alkyl group of the trialkylborane, followed by subsequent homolysis of the peroxide bond to form alkoxy radicals. Alkoxy radicals may then abstract hydrogen from an olefin surface. Our conclusions are based on experiments with model compounds and results from theoretical modeling.

Experimental Section

Organoboranes, 2,5,10,14-tetramethylpentadecane (pristane), heptadecane, and maleic anhydride were obtained from Aldrich Chemical (Milwaukee, WI). Grafting of the maleic anhydride was performed by combining maleic anhydride and pristane or heptadecane in a glass vial in equimolar amounts. The maleic anhydride was suspended in solution using a glass-encased magnetic stirrer. An equimolar amount of organoborane was withdrawn through a silicone rubber septum with a syringe and a fine gauge needle. The needle tip was then submerged under the surface of the pristane (or heptadecane) maleic anyhdride suspension and slowly injected with moderate agitation. Trialkylboranes, especially triethylborane (TEB), are pyrophoric in contact with air, and special care must be exercised in its handling. In general, we found that the use of a fine gauge needle with a nitrogen gap at the syringe front (from the trialkylborane blanket in the container) was adequate to prevent mishap. Upon introduction of the trialkylborane into the solution, the maleic anhydride over a period of minutes completely dissolved into the pristane solution. The solution formed a second phase. A denser phase was a dark yellow viscous liquid, while the less viscous upper phase was pale yellow. In general, the two phases contained the same products but at different concentrations. Significant heat was generated through the course of this transformation, but gram scale quantities could still be handled safely. Substitution of a borane ester such as diethylmethoxyborane (DEMOB) for the trialkylborane resulted in no detectable heat generation and no visual evidence for reaction.

Samples from the reaction mixture were diluted in acetonitrile. Gas chromatography and mass spectrometry (GC/MS) measurements were performed on an Aglilent 6890N GC coupled to a Micromass GCT, SN CA095, time-of-flight MS system operating in the electron impact (EI) and positive ion chemical ionization (PCI) modes. Conditions were as follows: column: 15 m × 0.25 mm i.d. × 0.25 μm film Rtx-5 SILMS; temperatures: column: 35 °C/hold 5 min to 275 °C at 10 °C/min; injector: 280 °C GC; reentrant: 280 °C; source: 180 °C (EI), 120 °C (PCI); flow: column: 1.5 mL/min; helium split: 300:1; detector: MCP: 2700V mode: +TOFMS, CENT; resolution: 9000 (at m/z 614); electron energy: 70 eV (EI), 100 eV (PCI); trap current: 150 μA (EI); scan: 25−400 amu (EI), 65−800 amu (PCI); rate: 0.3 s per scan; lock mass 201.9609 C_6F_5-Cl.

Solution polymerization of PMMA using organoborane initiators was performed in toluene at a 50 vol % concentration.

---

* Corresponding author.

10.1021/ma040095f CCC: $27.50

The mixture was mixed with a glass encased magnetic stirrer. Organoborane at the indicated molar concentration was introduced into the solution as before and the glass vial capped to prevent evaporation of the acrylic monomer or solvent. Size exclusion chromatography was performed on these solutions using 0.01 g of the polymer solution diluted in 10 mL of THF eluent. Chromatography was performed with a Waters model 510 at a nominal flow rate of 1 mL/min on an injected volume of 50 μL. Detection was performed using a Kratos Spectroflow 773 UV absorption detector set at 260 nm. Data analysis was performed using Polymer Laboratories Calibre GPC/SEC, acquisition version 6.0 and reanalysis version 7.04. The calibration was determined using narrow molecular weight distribution polystyrene standards from Polymer Laboratories.

Results and Discussion

Durable adhesion to polyolefins can be obtained by increasing the surface energy by one of several means listed above or, alternatively, by directly grafting polymer chains to the substrate surface.[18−21] One approach to this method is to utilize radical chemistry that can, in principle, abstract hydrogen atoms and provide a radical initiation site from which a radical chain reaction can commence. In the past, there have been several barriers to using radical chemistry to achieve this end. One such barrier is that carbon-centered radicals are generally not energetic enough to achieve substantial hydrogen abstraction. Alkoxy radicals are more suitable for abstraction of hydrogen.[22] However, generation of alkoxy radicals generally requires decomposition of peroxide bonds at elevated temperatures which usually sets up an unfavorable competition between homopolymerization of adhesive monomer and hydrogen abstraction/chain propagation.

Trialkylboranes are well-known generators of room temperature radicals[23] and can be pyrophoric when exposed to the atmosphere, depending on the attached alkyl groups.[24] A proposed mechanism of borane oxidation involves a diffusion-controlled reaction with oxygen.[25]

$$R_3B + O_2 \rightarrow R_2BO_2^{\bullet} + R^{\bullet} \quad (1)$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \quad (2)$$

$$RO_2^{\bullet} + R_3B \rightarrow R_2BOOR + R^{\bullet} \quad (3)$$

An alternative oxidation mechanism[26] of the borane proceeds with the oxygen inserting in a concerted fashion between a boron−carbon bond, skipping the generation of intermediate radical, resulting directly in the boron-containing peroxide (first product in eq 3).

$$R_3B + O_2 \rightarrow R_2BOOR \quad (4)$$

$$R_2BOOR \rightarrow R_2BO^{\bullet} + RO^{\bullet} \quad (5)$$

Applied to eqs 1−3, a steady-state assumption yields eq 6 for the total radicals concentration:

$$[R^{\bullet}] = \sqrt{\frac{k_{\mathrm{rad}}[R_3B]^2[O_2]^2}{k_t}} \quad (6)$$

where k_{rad} is the overall effective rate constant for production of initiator radicals and k_t is the rate constant for bimolecular chain termination. Given that molecular weight theoretically varies as the inverse of [R$^{\bullet}$] and assuming termination to occur primarily by recombination, the molecular weight should follow the simple form of eq 7 via eqs 1−3, where M_n is the number-average molecular weight and I is the normalized concentration of initiator species.

$$M_n \propto \frac{1}{\sqrt{[O_2]^2[R_3B]^2}} \propto \frac{1}{[I]} \quad (7)$$

For the mechanism of eq 4, the relevant reaction producing initiator is eq 5. This path leads to a molecular weight dependence on initiator level characterized by eq 8.

$$M_n \propto \frac{1}{\sqrt{[O_2][R_3B]}} \propto \frac{1}{\sqrt{[I]}} \quad (8)$$

The use of trialkylboranes for vinyl polymerizations has been described in the literature and the sensitivity of the polymerization to oxygen quantified.[26]

The very high room temperature reactivity of trialkylboranes can be mitigated by reaction of the borane (a Lewis acid) with a Lewis base.[27] Primary amines have typically been employed in this function and can produce complexes with the trialkylboranes that are stable solids or liquids at room temperature. When trialkylborane−amine complexes are included in adhesive compositions and the amine is subsequently deblocked from the trialkylborane by reaction with an acid, an isocyanate, or an aldehyde for instance, radical chemistry initiates room temperature vinyl polymerization and chain grafting to the polyolefin surface. It has previously been reported that alkoxydialkylboranes are nearly as effective as trialkylboranes in promoting vinyl polymerizations.[28] However, when an alkoxydialkylborane is used in adhesive formulations, polymerization is observed, but no adhesion is measured by any of several standard adhesion tests.

The mechanism differences by which trialkylboranes promote polymerization and adhesion while alkoxydialkylboranes promote only polymerization provides a basis for understanding these new adhesion promoting catalysts and their mode of action. Measurement of polymer molecular weight as a function of radical initiator concentration is a conventional way of providing insight into the concentration and composition of initiator species. Plots of 1/(number-average molecular weight) vs [I] for the mechanism of eqs 1−3 or vs $\sqrt{[I]}$ for the mechanism of eqs 4 and 5 should yield slopes reflecting the efficiency of radical generation. Figure 1 shows that tributylborane (in this case) produces a much greater number of radical initiators than DEMOB since the slopes are quite different. Further, methyl methacrylate polymerizations in toluene polymerized with either tri-*n*-butylborane (TBB) or diethylmethoxyborane yielded M_w/M_n of 2 ± 0.2, suggesting that the polymerization itself is unaffected by the initiating radicals as once reported[29] and that chain termination is not limited to radical recombination. A comparison of the data fit for the two plots does not lead to a clear preference for either model, but the fit is marginally better for the mechanism with a square root dependence on [I] as predicted by eqs 4 and 5 (Figure 1B).

Experiments on model compounds were performed to determine whether trialkylboranes and alkoxydialkylboranes could produce similar products in controlled experiments and whether the resultant products or

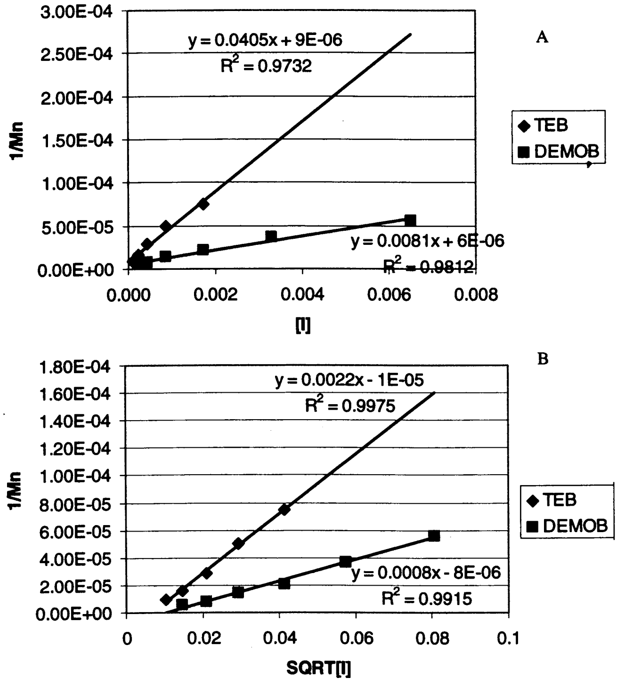

Figure 1. Inverse relationship between number-average molecular weight and molar concentration of radical initiators normalized to concentration of monomer. The fit of data is not sufficiently different to distinguish between the alternative oxidation mechanisms but is slightly better for the mechanism described by eqs 4 and 5.

product distributions were different. The compound 2,6,10,14-tetramethylpentadecane (“pristane”) is a useful model for polypropylene, and maleic anhydride (MAH) is a grafting vinyl monomer particularly useful in this experiment since it will not homopolymerize. Thus, the graft reaction of MAH and pristane results in products with well-characterized structures and molecular weights. When TEB is used to graft MAH to pristane, the total ion chromatogram (TIC) of Figure 2 is observed with the resulting products determined by mass spectrometry. Figure 2 shows that TEB is efficient at grafting MAH to pristane, and there is a slight preference for grafting to the 2-position relative to the 6-position—presumably a result of steric availability. All of the borane found in this system is accounted for in the peak at 3.82 min as triethylboroxine. The large peak at 13.97 min is unreacted pristane, and the peak at 9.02 min is the reaction product of MAH with two ethyl radicals. The peak at 6.31 min represents the reaction product of a single ethyl radical with MAH.

The presence of butanol has been observed in headspace measurements of similar systems (with TBB), confirming that alkoxy radicals are generated and are available for abstraction from hydrocarbon substrates such as pristane. Also indicating the presence of alkoxy radicals is the presence of diesters of maleic acid captured in the small peaks between 10 and 12 min, materials that are not detected with DEMOB initiation. The fact that only boroxine is present as a product of borane reactions suggests that borane undergoes only a single oxidation with O_2 and that the cyclic structure is preceded by homolysis of the peroxide structure. Trimerization of the singly oxidized material with the concomitant production of alkyl radical completes the sequence (vide infra). The results strongly indicate that the initiation and propagation reactions cascading from eq 3 or 5 are then

$$\mathrm{RO}^\bullet + \mathrm{R'{-}H} \rightarrow \mathrm{ROH} + \mathrm{R'}^\bullet \qquad (9)$$

$$3\mathrm{R_2BO}^\bullet \rightarrow \mathrm{R_3B_3O_3} + 3\mathrm{R}^\bullet \qquad (10)$$

$$\mathrm{R}^\bullet + n\mathrm{M} \rightarrow \mathrm{RM}_n^\bullet \qquad (11)$$

$$\mathrm{R'}^\bullet + n\mathrm{M} \rightarrow \mathrm{R'M}_n^\bullet\ \text{(adhesion)} \qquad (12)$$

$$\mathrm{R'}^\bullet + \mathrm{RM}_n^\bullet \rightarrow \mathrm{R'M}_n\mathrm{R}\ \text{(adhesion)} \qquad (13)$$

where R′ represents an organic substrate and M is the polymerizable monomer.

However, with the large amount of alkyl radical produced from these reactions it is also possible that another pathway is available following eq 2[22]

$$2\mathrm{RO_2}^\bullet \rightarrow \mathrm{ROOOOR} \qquad (14)$$

$$\mathrm{ROOOOR} \rightarrow 2\mathrm{RO}^\bullet + \mathrm{O_2} \qquad (15)$$

the products of which would then proceed as described above.

In this series of reactions, the alkoxy radicals are proposed to be responsible for hydrogen abstraction from the substrate, yielding a carbon-centered radical capable of initiating polymerization (eq 12) or terminating a growing chain (eq 13).

The disparity between mechanisms described by eqs 1−3 and eqs 4 and 5 is readily probed by modern computational techniques. The results of this analysis point to the direct insertion of oxygen between carbon and boron (eq 4) being the favored mechanism (Figure 3B). The calculations were carried out using density functional theory[30,31] and the 6-31G* basis set (B3LYP//6-31G*) contained in the SPARTAN program.[33] The peroxide formed via eq 3 or 4 should be stable given a dissociation energy of ca. +29 kcal/mol, yet we observe that the radicals formed, and the resulting adhesion occur readily at room temperature.[33] However, the calculations reveal that initial formation of the peroxide releases more than enough energy (−55 kcal/mol) to subsequently homolyze the oxygen bond. The fact that amine is not required to produce adhesion (acting as an inducer of the homolysis reaction) suggests that the release of energy is at least somewhat adiabatic. We also found that formation of the trialkylboroxine (eq 10) resulting in alkyl radical initiator is exothermic by 80 kcal/mol, consistent with the reaction products found in Figure 2.

The same experiment performed with diethylmethoxyborane (DEMOB) resulted in the TIC presented in Figure 4. The product distributions with TEB and DEMOB are strikingly different. The chromatogram shows the maleic anhydride adduct to pristane is formed, but only in trace amounts when catalyzed by DEMOB. In the chromatogram the peak at 12.13 min is unmodified pristane, and 13.1, 15.92, and 20.36 min are pristane impurities (impurities in pristane were unique from bottle to bottle but were alkanes). Most of the detectable borane in the DEMOB system gets tied up in the reaction of an ethylmethoxyboroxy radical with MAH (8.52 min). Surprisingly, some of the borane is again tied up in triethylboroxine (2 min) despite the fact the B−O bond is more stable than the B−C bond.[34] No trialkylborane was detected in the DEMOB sample. This suggests the reaction of an ethyl radical to dem-

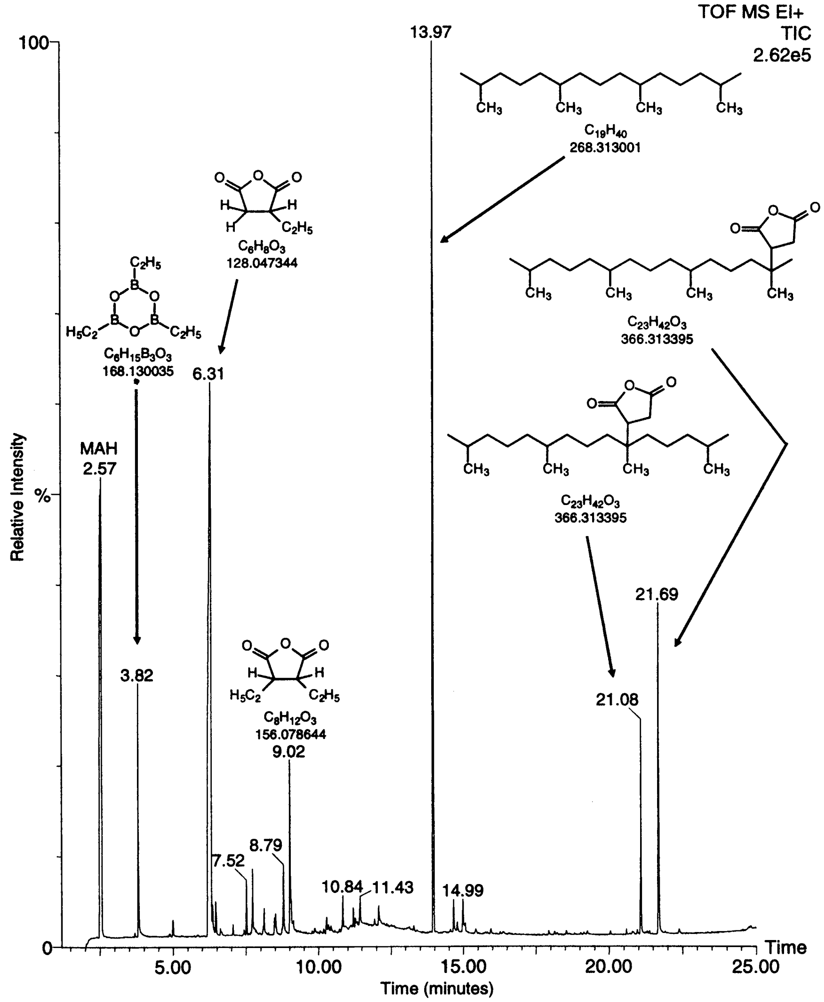

Figure 2. TIC of products resulting from the reaction of pristane, MAH, and TEB.

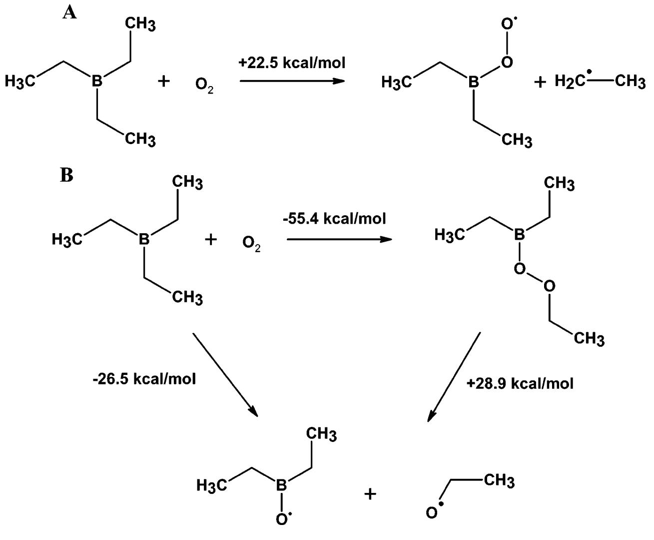

Figure 3. Calculated energies for the reaction path from trialkylborane and oxygen to radicals using two mechanisms proposed in refs 25 and 26, respectively. A positive number signifies an endothermic reaction while a negative number corresponds to an exothermic process. The mechanism in B is energetically favored.

ethylate DEMOB and form an ether (lost to the headspace) and a diethylboroxy radical. The stepwise reaction of this material with successive demethylated DEMOB molecules ends with the intramolecular cyclization to form the boroxine. In fact, the methyl radical has been trapped by experiments using TEMPO as a radical trapping agent.

Employing the same bond energy calculations as before reveals that the dissociation energy of the peroxide formed by insertion of oxygen between a B−C bond of DEMOB is favored but substantially less (by ca. 12 kcal/mol) than the same dissociation of the peroxide formed from a trialkylborane (Figure 5). This difference is presumably responsible for the fact that the same reactions are available to DEMOB for grafting, but the occurrence of such reactions is much less. The virtually inert dialkoxyboranes are reduced an additional 10 kcal/mol in energy change through peroxide homolysis.

These experiments show that the unexpected room temperature adhesion to polyolefin surfaces with no surface pretreatment can be ascribed to previously well-characterized radical processes that occur within a fortuitous window of conditions. While the exact sequence by which radical fragments get to their eventual products is not known with specificity, calculations strongly suggest that the preferred mechanism of borane oxidation occurs initially with oxygen insertion. The fragments themselves are reasonable byproducts of the basic reactions described by the equations. The implications of this result to other systems such as peroxymerics,[29] metal alkyls,[35,36] and reactions with cocatalysts[29] achieving a similar result are clear.

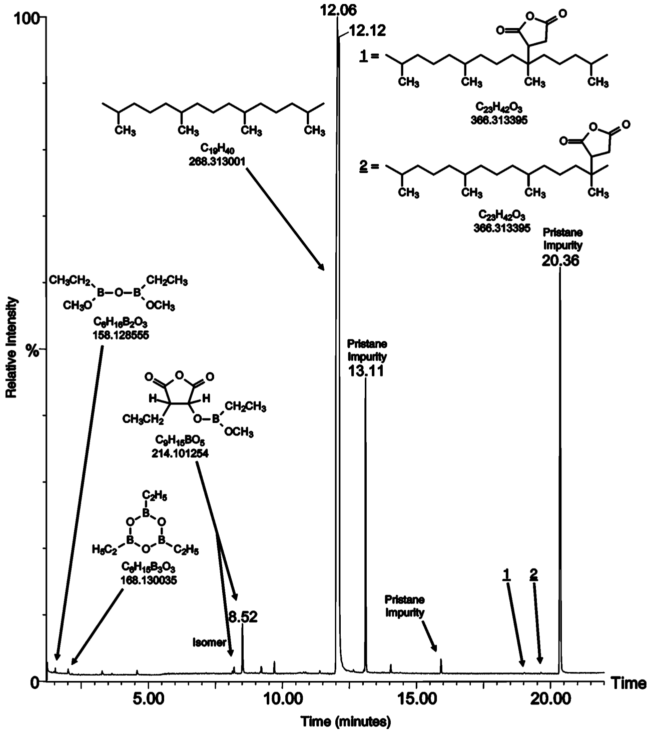

Figure 4. GC chromatogram of reaction product of DEMOB with MAH and pristane. Reaction and measurement conditions are the same as in Figure 2. Very little heat was generated by the mixing of DEMOB into the pristane−MAH mixture, however.

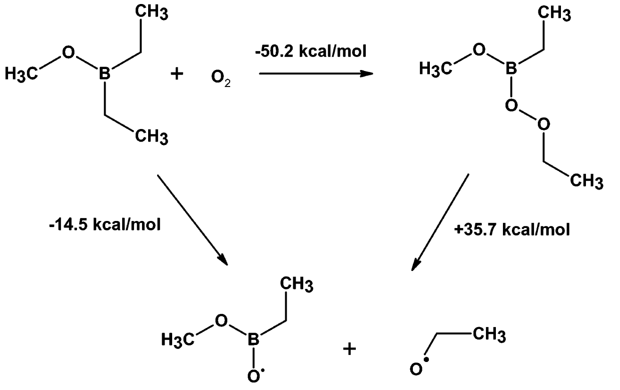

Figure 5. Energetics of the formation of radical products from the reaction of oxygen with DEMOB assuming the energetically favored oxygen insertion mechanism of Figure 3B. The reaction to products is favored but substantially less so than the reaction of TEB.

Acknowledgment. We acknowledge Dr. Ray Drumright for helpful discussions and Dr. David Meunier for molecular weight measurements.

Supporting Information Available: A compendium of TIC and mass spectral analyses based on fragmentation patterns for all experiments mentioned in this article. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Brewis, D. M.; Briggs, D. *Polymer* **1981**, *22*, 7−16.
(2) Pocius, A. V. *Adhesion and Adhesives Technology*; Hanser: Munich, 1997; pp 183−214.
(3) Rauhut, H. W. *Adhes. Age* **1969**, *12*, 28−38.
(4) Devine, A. T.; Bodnar, M. J. *Adhes. Age* **1969**, *12*, 35−37.
(5) Clemens, R. J.; et al. *Prog. Org. Coat.* **1994**, *24*, 43−54.
(6) Badey, J. P.; et al. *Int. J. Adhes. Adhes.* **1996**, *16*, 173−178.
(7) Schonhorn, H.; Hansen, R. H. *J. Appl. Polym. Sci.* **1967**, *11*, 1461−1474.
(8) Westerdahl, C. W.; Hall, J. R.; Schramm, E. C.; Levi, D. W. *J. Colloid Interface Sci.* **1974**, *47*, 610−620.
(9) Blais, P.; Carlsson, D. J.; Csullog, G. W.; Wiles, D. M. *J. Colloid Interface Sci.* **1974**, *47*, 636−649.
(10) Schmitz, P. J.; Holubka, J. W. *J. Adhes.* **1995**, *48*, 137−148.
(11) Brewis, D. M.; Mathiewson, I.; Wolfsenberger, M. *Int. J. Adhes. Adhes.* **1995**, *15*, 87−90.
(12) Yang, J.; Garton, A. *J. Appl. Polym. Sci.* **1993**,*48*, 359−370.
(13) (a)Sonnenschein, M. F.; Webb, S. P.; Rondan, N. U.S. Patent 6,706,831, 2004. (b) Sonnenschein, M. F.; Webb, S. P.; Rondan, N. U.S. Patent 6,713,578, 2004. (c) Sonnenschein, M. F.; Webb, S. P.; Rondan, N. U.S. Patent 6,730,759, 2004. (d) Webb, S. P.;. Sonnenschein, M. F. U.S. Patent 6,740,716, 2004. (e) Sonnenschein, M. F.; Webb, S. P.; Wendt, B. L.; Harrington, D. R. US Patent 6,762,260, 2004. (f) Sonnenschein, M. F.; Webb, S. P.; Wendt, B. L.; Harrington, D. R. U.S. Patent 6,777,512.
(14) Skoultchi, M. M.; Merlo, N. V. U.S. Patent 5,106,928, 1992.
(15) Zharov, J. V.; Krasnov, J. N. U.S. Patent 5,539,070, 1996.
(16) Maandi, E. U.S. Patent 6,632,908, 2003.
(17) Kendall, J. L.; Righettini, R. F.; Abbey, K. J. U.S. Patent 6,646,076, 2004.
(18) Pesetskii, S. S.; Jurkowski, B.; Makarenko, O. A *J. Appl. Polym. Sci.* **2002**, *86*, 64−72.
(19) Yamamoto, K.; Tanaka, H.; Sakaguchi, A.; Shimada, S. *Polymer* **2003**, *44*, 7661−7669.
(20) Bergbreiter, D. E.; et al. In *Polymer Surfaces and Interfaces: Characterization and Application*; Mittal; Lee, K.-W., Eds.; Van Nostrand: New York, 1997; pp 3−18.
(21) Bergbreiter, D. E.; Xu, G.-F.; Zapata, C. *Macromolecules* **1994**, *27*, 1597−1602.
(22) Ingold, K. U. In *Free Radicals*; Kochi, J., Ed.; Wiley: New York, 1973; Vol. 1, p 80.
(23) Ollivier, C.; Renaud, P. *Chem. Rev.* **2001**, *101*, 3415−3434.
(24) Ingold, K. U. In *Free Radicals*; Kochi, J., Ed.; Wiley: New York, 1973; Vol. 1, p 88.
(25) Brown, H. C.; Midland, M. M. *Chem. Commun.* **1971**, 699−700.
(26) Welch, F. J. *J. Polym. Sci.* **1962**, *61*, 243−252.
(27) Hoberg, H.; Gotz, V. *J. Organomet. Chem.* **1976**, *118*, C3−C5.
(28) Furukawa, J.; Tsuruta, T; Imada, T.; Fukatani, H. *Makromol. Chem.* **1959**, *31*, 122−139.
(29) Dudonov, V. A.; Grishin, D. F.; Aksenova, I. N *Polym. Sci.* **1993**, *35*, 1744−1746.
(30) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133.
(31) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.
(32) Spartan 2004, Wavefunction Inc., Irvine, CA.
(33) The reliability of these calculations is illustrated by comparing the calculated dissociation energy of diethyl peroxide 36.5 kcal/mol with the experimental value of 37.9 ± 1 kcal/mol. Cf.: Batt, L.; Christic, K.; Milne, R. T.; Summers, A. J. *Int. J. Chem. Kinet.* **1974**, *6*, 813.
(34) Midland, M. M.; Brown, H. C. *J. Am. Chem. Soc.* **1971**, *93*, 1506−1509.
(35) Ryu, I.; Araki, F.; Minakata, S.; Komatsu, M. *Tetrahedron Lett.* **1998**, *39*, 6335−6336.
(36) Bertrand, M. P.; Feray, L.; Nouguier, R.; Perfetti, P. *J. Org. Chem.* **1999**, *64*, 9189−9193.

MA040095F