Macromolecules **2006,** *39,* 2507−2513

Physical and Chemical Probes of the Bond Strength between Trialkylboranes and Amines and Their Utility as Stabilized Free Radical Polymerization Catalysts

Mark F. Sonnenschein,* Steven P. Webb, O. David Redwine, and Benjamin L. Wendt

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

Nelson G. Rondan

Corporate Research and Development, The Dow Chemical Company, Freeport, Texas 77541

Received February 3, 2006

ABSTRACT: Trialkylboranes are established polymerization catalysts in part due to their ability to generate radicals at room temperature when exposed to oxygen. This capability also creates the conditions for a fire hazard if the oxidation does not commence under controlled conditions. One way to achieve control of the catalyst reactivity is to react trialkylborane with an amine and so hinder the route by which oxygen initially interacts with the borane. Because of its dative nature, the borane−amine bond can be broken at relatively low temperatures; this temperature can be tuned by controlling the strength of the bond. This article details the electronic and structural amine features that result in more stable trialkylborane amine bonds, demonstrates several methods to physically probe the bond strength, and correlates the methods to each other. Last, the relationship of trialkylborane amine bond strength to catalyst and adhesion promoter efficacy is presented.

Introduction

Low surface energy plastics such as polyethylene, polypropylene, and poly(tetrafluorethylene) have a variety of attractive properties, generating a broad array of uses; however, because of their low surface energy, it is very difficult to find adhesive compositions to bond them.[1] Commercially available adhesives that are used for these plastics require time-consuming or extensive pretreatment of the surface before adhesive bonding can take place. Such pretreatments include corona treatment, flame treatment, high energy chemical oxidations, and priming for example.[2−10] The requirement for extensive pretreatment of the surface results in significant barriers to engineers and designers of structures that use plastics.

Recently, we[12] and others[13−17] have disclosed technology that provides very strong adhesion to polyolefins and fluorinated polymers at room temperature without the need for surface pretreatment. The technology employs conventional acrylic adhesive, but initiates polymerization with trialkylborane radical generators.[18,19] These catalysts react with adventitious oxygen to produce alkoxy and alkyl radicals capable of abstracting hydrogen from polyolefin substrates and initiating radical polymerization respectively as depicted in Scheme 1.[20] Adhesion is achieved by radical combination of the surface radical site with a growing polymer chain, or by direct initiation of acrylic polymerization by the carbon radical generated on the plastic surface following hydrogen abstraction by the alkoxy radical (eq 3).[21]

This article will describe synthesis, stability, and effectiveness of trialkylborane−amine catalysts useful for the promotion of adhesion to plastic substrates.

Experimental Section

All trialkylboranes, amines, acrylic monomers, and acrylic polymers used in this work were purchased from Aldrich Chemical (Milwaukee, WI) and used without further purification. Trialkylboranes were obtained at 1 M concentration in either THF or diethyl ether. Isotactic polypropylene was obtained from either grade 6524 from Montell (now Basell N.V.) or Dow Chemical (Grade H704−04).

Scheme 1. Reaction Pathway by Which Trialkylborane Promotes Adhesion to Polyolefin Surfaces[21]

$$R_3B + O_2 \longrightarrow R_2BOOR \qquad \textbf{(1)}$$

$$R_2BOOR \longrightarrow R_2BO^{\bullet} + RO^{\bullet} \qquad \textbf{(2)}$$

$$RO^{\bullet} + R'\text{-}H \longrightarrow ROH + R'^{\bullet} \qquad \textbf{(3)}$$

$$3R_2BO^{\bullet} \longrightarrow R_3B_3O_3 + 3R^{\bullet} \qquad \textbf{(4)}$$

$$R^{\bullet} + nM \longrightarrow RM_n^{\bullet} \qquad \textbf{(5)}$$

$$R'^{\bullet} + nM \longrightarrow R'M_n^{\bullet} \qquad \textbf{(6) adhesion}$$

$$R'^{\bullet} + RMn^{\cdot} \longrightarrow R'M_nR \qquad \textbf{(7) adhesion}$$

Trialkylborane complexes with diethyl ether (DEE) are stabilized through the interaction of the nonbonding ether oxygen with the unoccupied P orbital of boron much the same way borane is stabilized with amines.[22,23] However, since ethers are minimally basic and volatile, their borane complex is in equilibrium with uncomplexed components, and the material becomes progressively more pyrophoric as excess ether evaporates. Substitution of the ether with amine was performed under nitrogen and ice cooling to prevent ether from boiling since the formation of the borane−amine complex can result in a substantial exotherm. Prior to addition of amine to cooled borane-ether complex, the amine was sparged with nitrogen to reduce the dissolved oxygen concentration. The presence of dissolved oxygen has been shown to result in slow formation

10.1021/ma060268w CCC: $33.50

Table 1. Iodometric Determination of Peroxides[25] in Trialkylborane Complexes as a Function of Complex and Procedure[a]

sample	peroxide (ppm)
aged tributylborane in diethyl ether	729
tributylborane:methoxypropylamine using unsparged components	352
tributylborane:methoxypropylamine using fresh sparged components	23

[a] Aged ether complex is at least 4 months old.

of peroxidized boranes,[22] while exclusion of oxygen results in minimal oxidation (Table 1). The reaction of trialkylborane with amine proceeds under flowing N_2. The excess ether was removed with a laboratory rotovap. Up to 30% molar excess of amine was used in substitution to ensure complete exchange of the ether and allow for any evaporation during removal of ether under vacuum. The speed of reaction depends on the free energy change of the substitution reaction involved; but in these experiments the reaction was allowed to proceed for between 30 and 60 min.

Pyrophoricity of trialkylborane complexes can be determined qualitatively in a chemical hood by placing a small (milligram) amount of liquid or solid complex onto a dry paper towel and observing if the paper smokes or smolders. Any ignition can be easily extinguished with water. Burning or smoldering of the paper indicates a pyrophoric product, while discoloration of the paper might be considered "slightly" pyrophoric.

The use of acrylic resins for adhesives is well-known and many have been successfully used in this research to create durable bonds to low surface energy plastics. For the purpose of describing the current research, a very simple two component composition was applied. In one component (side "A") was trialkylborane−amine complex, and acrylic monomers that do not react with amines. The second (side "B") was composed of acrylic monomers and a component that readily reacts with amines, such as a Bronsted or Lewis acid, an isocyanate, an aromatic aldehyde or some hydroxyl containing acrylic monomers (reacting via a Michael addition). In the current experiments trialkylborane was liberated by including acrylic acid in the B side to react with the amine. The weight of acrylic acid was between 2 and 4% of the total adhesive mass. The thixotropy of the system was controlled by dissolving poly(methyl methacrylate) or methacrylate copolymers into the unreacted monomer. In the current experiments thixotropy was controlled by addition of 300 000 Da poly(methyl methacrylate) (PMMA) to methyl methacrylate in the weight ratio of 16:84. The two sides were kept separate until ready for application. The two sides were combined such that total alkylborane was between 1 and 3 wt % of the adhesive depending on the molecular weight of the borane and particular aspects of the alkyl groups attached to the boron (vide infra). A and B sides were mixed using either a dual component plunger with a static mixer, or in a weighing dish and mixed thoroughly with a spatula. Glass beads (3, 5, or 30 mil in diameter) were usually added in this step to ensure a uniform adhesive bead thickness to the adhesive structure. Results were not very sensitive to bead thickness, but lap shear strength was sometimes higher with thinner beads because of fewer defects in the adhesive film.[26] The mixed adhesive was then spread on unprepared substrate surface covering 1.6 cm^2 and assembled into lap shear geometry.

Adhesive samples were tested on an Instron tensile testing machine (model 4202) at 2.54 cm/min using Series 9 or Merlin data analysis software. Peroxide measurements on trialkylborane complexes were made using an iodometric method used for measuring peroxides in glycol ethers.[25] Trialkylborane amine complex energies and amine electrostatic potentials (ESP) were calculated using density functional theory and the 6-31G** basis set (B3LYP//6-31G**) contained in the Spartan program.[27,28] The reported ESP[29] represents the maximum calculated for the isolated molecule. Dissociation temperatures were measured by placing 2 wt % of trialkylborane−amine complex into acrylic resin described above. Temperature dependent viscosity (thermoviscometry) of this solution was then measured using the thermal cell of a calibrated Brookfield III digital viscometer. In the current experiments Brookfield spindle 34 was employed at 50 rpm and the temperature ramp was approximately 2 °C/min. The "decomplexation temperature" is the temperature reading from the Brookfield thermocell at which the viscosity had increased at least 10% from its lowest value. This measurement was reproducible with a deviation of ±2 °C. An independent measurement of trialkylborane−amine complex thermal stability was obtained from differential scanning calorimetry (DSC) measurements in air at 10 °C/min using a TA Instruments model 2900 DSC. The dissociation of stable complex followed by oxidation of the trialkylborane was highly exothermic and easily observed. A final method of determining the stability of the trialkylborane−amine complex was obtained by measuring the chemical shift of the ^{11}B nucleus by nuclear magnetic resonance spectroscopy (NMR). ^{11}B NMR was performed at 192 MHz using a Varian INOVA 600 MHz spectrometer with a Nalorac Z-spec 10 mm BBSI boron background-free probe and 8 mm PTFE tubes. Spectra were obtained at 22 °C with a relaxation delay of 0.5 s, an observe pulse of 30 degrees, acquisition time of 0.07 s, and a spectral width of 58.6 kHz. Then128 free induction decays were signal averaged for each spectrum. Spectra were apodized with a 20 Hz exponential prior to Fourier transformation. Chemical shifts were referenced to an external standard containing BF_3−diethyl ether dissolved in toluene-d_8.

Results and Discussion

Trialkylboranes are aptly characterized as high energy materials.[30] Their diffusion limited oxidation and subsequent copious production of radicals makes them relatively pyrophoric in the presence of oxygen. The control of this oxidation is crucial to the safe laboratory use of trialkylboranes and their application as catalysts and adhesion promoters. As described in the Experimental Section, control begins by eliminating oxygen from the complexation environment. However, the strength of the trialkylborane−amine acid−base complex affects both the resulting safety of the complex and also its efficacy as a catalyst.

Since there is no direct method of measuring Lewis basicity[31,32] (as opposed to Bronstead basicity[33]), an alternative for evaluating the strength of trialkylborane−amine complexes is to calculate the binding energy of the complex.[34] The stability of the complex can be determined from the energy difference between the trialkylborane−amine complex and the sum of energies of the isolated Lewis acid (trialkylborane) and base (amine). The difference is known as the binding energy. The higher the binding energy the more stable the complex.

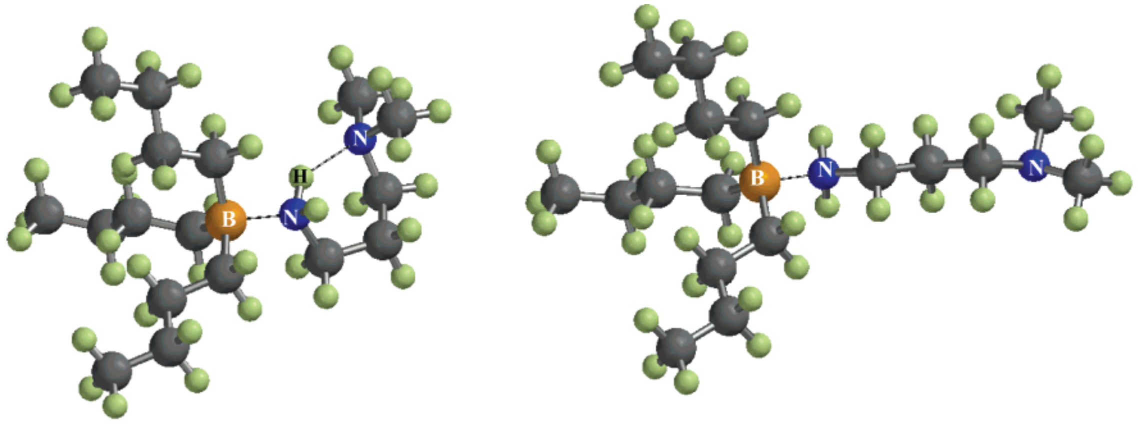
$$\text{binding energy} = -(\text{complex energy} - (\text{energy of Lewis acid} + \text{energy of Lewis base})) \quad (8)$$

Such binding energies can be calculated using theoretical ab

Table 2. Calculated Binding Energies, Bond Distances of Tri-*n*-butylborane with Various Amines and the Maximum Electrostatic Potential of the Isolated Amines (ESP)[a]

example	amine	binding energy (kcal/mol)	B−N bond length (Å)	ESP (kcal/mol)
1	dimethylaminopropylamine cyclic complex	15.8	1.706	−54.5
2	dimethylaminopropylamine linear complex	13.3	1.728	−49.1
3	methoxypropylamine cyclic complex	15.5	1.712	−54.0
4	methoxypropylamine linear complex	13.4	1.729	−50.9
5	propylamine	13.2	1.73	−49.1
6	triethylenediamine (DABCO)	6.1	1.85	−42.8
7	pyridine	8.1	1.727	−45.2
8	4-(dimethylamino)pyridine	11.4	1.710	−51.5
9	imidazole	11.1	1.646	−52.9
10	aziridine	12.4	1.707	−48.3
11	azetidine	14.3	1.698	−47.2
12	pyrrolidine	12.3	1.733	−45.2
13	piperidine	10.5	1.768	−42.7
14	trimethylamine	1.7	1.870	−39.7
15	triethylamine	0.0	NA[b]	−38.6
16	hexamethylenediamine cyclic complex	14.9	1.727	−54.1
17	hexamethylenediamine linear complex	14.1	1.703	−49
18	aminopropylmorpholine cyclic complex	12.1	1.705	−52.4
19	aminopropylmorpholine linear complex	10.7	1.725	−48.5
20	α-methylbenzyamine	10.5	1.735	−46.5
21	dibutylamine	6.2	1.78	−44.3
22	dipropylamine	6.1	1.768	−43.5
23	ethanolamine cyclic complex	13.7	1.719	−51.2
24	ethanolamine linear complex	11.8	1.737	−45.2
25	*N*-(3-aminopropyl)propanediamine	16	1.697	−58.4
26	morpholine	9.90	1.78	−43
27	isophorone diamine (*trans*-3-aminomethyl)	13.14	1.724	−47.6
28	isophorone diamine (*trans*-1-amino)	11.73	1.726	−46.5
29	isophorone diamine (*cis*-3-aminomethyl)	12.33	1.727	−47.4
30	isophorone diamine (*cis*-1-amino)	11.08	1.725	−46.3

[a] Examples 27−30 represent different conformations the isophorone diamine may assume. [b] NA = not applicable due to lack of a binding energy.



TBB-DMAPA cyclic conformation TBB-DMAPA linear conformation

Figure 1. Diagram of the cyclic and linear conformations of tributylborane with dimethylaminopropylamine. The energy reduction in the cyclic conformation suggests that almost all of the complex will be present in the cyclic state.

initio methods employing commercial software packages such as described in the Experimental Section. Table 2 provides the results from calculations made on selected trialkylborane−amine complexes.

The representative results of Table 2 show that the conformation certain amines can assume provides additional stability to the complex. For example, the binding energy of the cyclic complex of tributyl borane with methoxypropylamine is an additional 2.1 kcal/mol more stable than the linear complex. Intramolecular hydrogen bonding of the oxygen nonbonding electrons to hydrogen of the amine group increases the basicity of the amine. Similar results are observed with aminopropylmorpholine and dimethylaminopropylamine (Figure 1). All linear conformations of primary amines result in a stabilization energy of about 13 kcal/mol. As will be shown later, calculated binding energies of less than 11 kcal/mol are weak enough that there is a risk of pyrophoricity at room temperature. There is also a calculated trend of enhanced stabilization for cycloaliphatic amines (3−6 ring atoms, examples 10−13) with a maximum at four ring atoms (azetidine). The calculations also suggest that linear secondary and tertiary amines form weak complexes. This is almost entirely a result of steric hindrance rather than enthalpic effects, since in the case of secondary amines that possess less steric obstruction such as pyrrolidine (no. 12), relatively strong bonds are possible. Finally there is a correlation between binding energy and the calculated bond length and the relatively more easily calculated amine electrostatic potential. Although the correlation (r^2 of ∼0.7 and ∼0.6

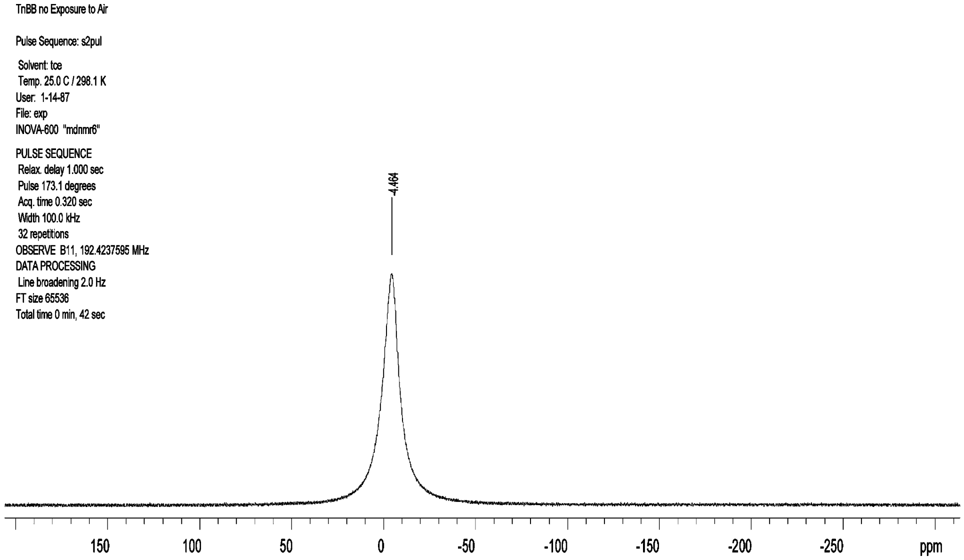


Figure 2. ^{11}B spectrum of tri-*n*-butylborane−dimethylaminopropylamine at 25 °C.

Table 3. ^{11}B NMR Resonance Peak Position of Alkylborane−Amine Complexes, with All Measurements at 25 °C unless Otherwise Noted[a]

borane−amine complex	shift (ppm)
TBB−hexamethylenediamine	−4.4
TBB−dimethylaminopropylamine	−4.8 −5.4 (10 °C)
TBB−aminopropylmorpholine	−7.7
TBB−α-methylbenzylamine	−1.49
TBB−dibutylamine	0.48
TBB−dipropylamine	0.73
TOB−dimethylaminopropylamine	−5.82
TBB−*N*-(3-aminopropyl)propanediamine	−7.05
TBB−ethanolamine	−3.49

[a] TBB = tri-*n*-butylborane, and TOB = tri-*n*-octylborane.

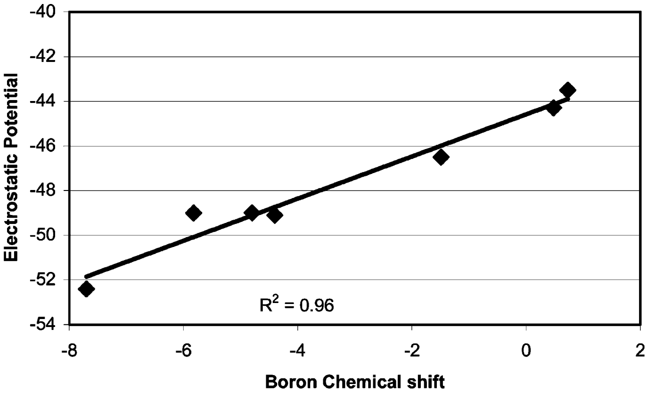


Figure 3. Relationship between calculated electrostatic potential taken from Table 2 and boron chemical shift taken from Table 3 for mono- and diamines.

respectively) is not ideal, the trend is unmistakable (data are provided in Supporting Information). Thus, much information about the complexes can be obtained simply from consideration of the amine properties.

An alternative method to assess borane−amine complex stability is to measure the ^{11}B chemical shift. Spectra show that tri-*n*-butylborane complexed with amine exhibits a so-called "anion shift" resulting from the electron density of the amine being donated to the empty boron P orbital.[35] Table 3 provides the observed boron anion shift for several complexes; a more negative value indicates greater electron density on the boron due to stronger interactions with the complexed amine. This method is also a useful detector of the presence and amount of oxidized components as shown in the Supporting Information. It is interesting and useful to note that there is a strong relationship between the boron chemical shift and the relatively easily calculated amine electrostatic potential maximum, particularly for the comparison of mono- and diamines complexed to tributylborane (Figure 3).

The translation of quantum mechanical calculations and indirect measures of complex stability (such as NMR chemical shifts) with direct measures of complex stability requires recognition that actual measurements may exhibit variability due to uncontrolled factors. These include the ambient concentration of oxygen, the occurrence of radical inhibitors or scavengers, and other systematic sources of error. However, the trends observed by various direct methods are consistent with the more thermodynamic techniques described above.

The thermally activated deblocking of Lewis acids from Lewis bases is well-known and commonly practiced.[36] For instance the deblocking of amines from carboxylic acids is often employed in polyurethane foaming to control the timing and competition of the gas forming and polymer gelling reactions.[37] Similarly, boron trifluoride−ethylamine complex is reversible with a deblocking temperature about 90 °C at which point the very strong Lewis acid boron trifluoride is released. The similarity of the trialkylborane−amine complexes to these systems suggests that it may be possible to detect the deblocking of the amine thermally. DSC can detect the release of bond enthalpy, subsequent rapid oxidation of borane, and also quantify the amount of heat generated by the processes. Figure 4 provides a representative thermogram of tri-*n*-butylborane complexed with methoxypropylamine. Table 4 gives the decomposition temperatures for a variety of borane complexes.

A wide range in enthalpy per gram was measured for the complexes, to some extent reflecting the difference in molecular weight of the complex (for instance the difference between dimethylaminopropylamine with tri-*n*-butyl and tri-*n*-octylborane), and in the case of hexane diamine, a low equivalent weight of the amine. Some variance was also probably a result of oxidation of the samples resulting from the varying age of the samples. In the case of pyrophoric borane−amine complexes, no enthalpy of reaction was observed in these experiments that began ostensibly at room temperature. Even if no exotherm was observed, the endotherm from boiling of tributylborate was still observed. Subsequent scans on samples

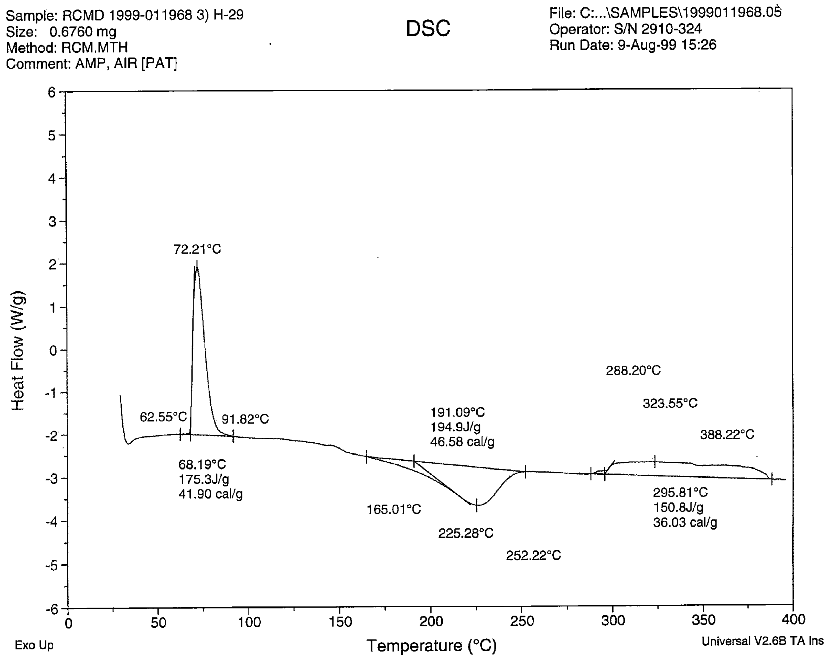


Figure 4. DSC trace of the decomposition and oxidation or tri-*n*-butylborane:methoxypropylamine complex in air. The endotherm peaking at 225 °C is volatilization of the tributylborate.

Table 4. Representative Data from DSC for Room Temperature Stable Amine Complexes with Tri-*n*-butylamine

amine	dec temp (°C)
aminopropylmorpholine	62.5
dimethylaminopropylamine[a]	72.6
dimethylaminopropylamine	73
isophoronediamine	72
hexamethylenediamine	52.7
propylamine	55
pyrrolidine	73
aminopropanol	72
methoxypropylamine	72
aminopropylpropanediamine	71

[a] Complex with tri-*n*-octylborane.

showed no transitions. Enthalpy data are included in the Supporting Information.

Another direct measurement of catalyst stability can be obtained by measuring the temperature at which the catalyst complex causes monomer to polymerize. Radical polymerizations tend to be rapid, and continuous monitoring of monomer viscosity with temperature gives a direct indication of thermal stability. Experiments monitoring radical initiation and subsequent polymerization yielded results typified by those shown in Figure 5. Both samples initially exhibited decreasing viscosity with increasing temperature until a point that the trialkylborane–amine complex deblocked, and subsequent oxidation and radical formation resulted in polymerization as measured by increasing viscosity.

Measurement of temperature at which catalyst complexes initiate polymerization is about 15 °C below the peak exotherm temperatures and about 10 °C below the beginning exotherm temperatures measured by DSC. This suggests that either decomposition of catalyst is affected by the chemical environment in which it finds itself, or the time constant of DSC measurement is too long to accurately detect the onset of decomposition/oxidation (i.e., the temperature of the DSC is rising faster than the differential amplifier can detect the chemical process beginning). Within the current data gathering procedures, direct measurement of the onset of monomer polymerization has the advantage of detecting somewhat less stable complexes, requiring the least instrumental sophistication, and providing direct information on the property in question (thermal stability). The relationship between data received by the various methods is relatively good, and the availability of only one technique could be used for the purpose of establishing trends.

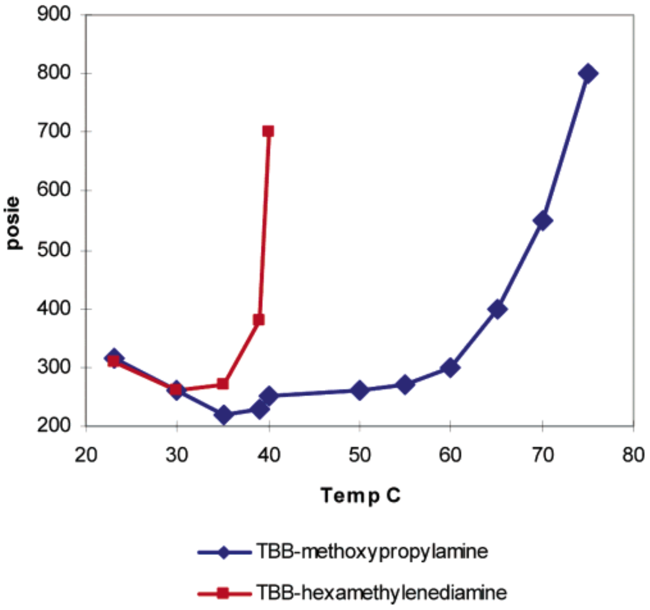


Figure 5. Temperature dependent viscosity of 83% methyl methacrylate, 15% 300 000 Da PMMA with 2% (wt) of the indicated complex. The molecular weight difference between the complexes causes there to be a slight difference in the moles of borane in the systems, but the results were not measurably affected by the variance.

Figures 6 and 7 show that determining the stability of the catalyst complex in polymerizable monomer via thermoviscometry follows the same trends predicted from calculation of binding energies and from indirect measurement of bond strength (NMR chemical shift).

If the trialkylborane–amine bond is too weak, even at room temperature, the catalyst will have a lifetime that is insufficient

Table 5. Stability and Catalyst Efficacy of Trialkylborane Amine Complexes

borane	amine	molar B:amine	pyrophoric?	decomplexation temp (°C)	lap shear (on PP) (psi)
TBB	hexanediamine	1:1	N	40	>444
TBB	DMAPA	1:1.1	N	52	>900
TBB	DMAPA	1:1.2	N	53	>655
TPB	DMAPA	1:1.1	N	ND	0
TBB	aminopropylmorpholine	1:1.1	N	50	>682
TOB	DMAPA	1:1.3	N	ND	471
TBB	cyclohexylamine	1:1.2	sl	20	>933
TBB	aminopropanol	1:1.2	N	20	>624
TBB	morpholine	1:1.2	Y	20	>818
TBB	ethanolamine	1:1.17	N	42	458
TBB	piperidine	1:1.5	N	52	>783
TBB	pyrrolidine	1:1.4	N	ND	679
TiBB	pyrrolidine	1:1.4	N	ND	303
DEBM	DMAPA	1:1.25	N	68	36
DEBI	DMAPA	1:1.25	N	77	64
TBB	isophorone diamine	1:1.36	N	46	>893
TBB	methoxypropylamine	1:1.36	N	63	>640
TBB	*a*-methylbenzylamine	1:1.6	sl	25	451
TBB	aminopropylpropanediamine	1:1.2	N	64	>559
TBB	aminoethoxyethanol	1:1.3	N	25	>847
TOB	methoxypropylamine	1:1.3	N	68	110
TOB	aminopropanol	1:1.3	N	53	79
TBB	morpholine	1:3	N	42	>878
TBB	aminopropanol	1:2	N	60	>419
TOB	isophorone diamine	1:1.3	N	ND	0
TBB	diisopropylamine	1:2	Y	50	0
TBB	cyclohexylamine	1:2	N	30	508
TBB	piperidine	1:2	N	85	>775
TBB	aminoethoxyethanol	1:2	N	50	276
TBB	piperazine	1:1.3	N	20	>749
TBB	methyl pyrrolidinone	1:2	Y	20	0
TBB	tetrahydrothiophene	1:1.3	N	20	0
TBB	diethanolamine	1:2	Y	65	61
TBB	triethylamine	1:2	Y	52	0
TBB	dibutylamine	1:1.3	N	50	39
TBB	dipropylamine	1:1.3	Y	52	0
TBB	dioctylamine	1:1.3	N	58	192
TBB	DABCO	1:1.3	sl	25	>774
TBB	thiazolidine	1:1.3	Y	25	>725
TBB	thiazolidine	1:2	N	25	186
TBB	urea	1:1.3	Y		NA
TBB	1,8-diazabicyclo[5,4]undec-7-ene	1:1.3	N	ND	>842
TBB	4-dimethylamino pyridine	1:3	N	57	>581
TBB	proline methyl ester	1:1.3	N		0
TBB	4-bromo piperidine	1:1.3	Y		0
TBB	acetaldehyde ammonia trimer	1:1.3	sl	67	0
TBB	1-amino-4-methyl Piperazine	1:1.3	N	25	145
TBB	homopiperazine	1:1.3	N	25	638
TBB	2-(	1:3	sl	25	0
TBB	tetraazaadamantane	1:2	Y		0
TBB	hexylamine	1:1.3	N	45	>885
TBB	tetramethylguanidine	1:1.3	N	74	>616
TBB	tetrahydropyrimidine	1:1.3	N	75	>736
TBB	2-methyl-2-imidazoline	1:1.3	N	35	>1000

[a] Lap shear experiments in which the substrate broke prior to bond failure are denoted with a ">" sign. Key: TBB = tri-*n*-butylborane, TOB = tri-*n*-octylborane, DEBM = methoxydiethylborane, DEBI = isopropoxydiethylborane, TPB = triphenylborane, TiBB = tri-isobutylborane, DMAPA = dimethylaminopropylamine, Y = yes, N = no, and sl = slightly pyrophoric.

unless oxygen is meticulously excluded from the environment. Catalysts with borderline stability may have degraded performance as the catalyst ages. Similarly, catalysts with borderline performance may exhibit improved performance when the amine-to-boron ratio is increased, thus moving the equilibrium of reactants (complex) and product (decomplexed, trialkylborane and amine) toward the reactants. However, catalysts with borderline stability prepared with amines that are volatile or that chemically degrade to an even less stable remnant may become increasingly pyrophoric as the trialkylborane becomes unprotected.

Table 5 shows that catalysts that are stable and have decomplexation temperatures well above room temperature have good performance catalyzing polymerization of the adhesive monomer and promoting adhesion to isotactic polypropylene. Samples that upon introduction of alkylborane−amine to monomer at room temperature immediately commence radical chemistry in the absence of an amine reactive agent (decomplexation temperature ≤ 25 °C) may provide some adhesion if the oxidation does not proceed too quickly and if the catalyst is employed before it has aged to the point of inactivity. It is also shown in Table 5 that dialkylalkoxyborane (DEBI and DEBM) complexes with amines may provide relative stability preventing further oxidation, but their relative inactivity to oxygen prevents them from producing meaningful adhesion as predicted in our prior work.[21] Comparison of thermodynamic and spectroscopic calculations and measurements to observations of pyrophoricity suggest that complexes with binding energies

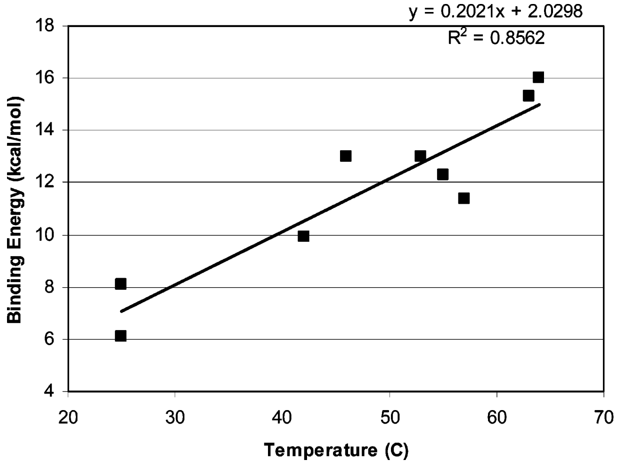


Figure 6. Calculated trialkylborane−amine binding energies for catalysts vs temperature at which the catalyst trialkylborane−amine bond thermally breaks as determined by the onset of acrylic polymerization.

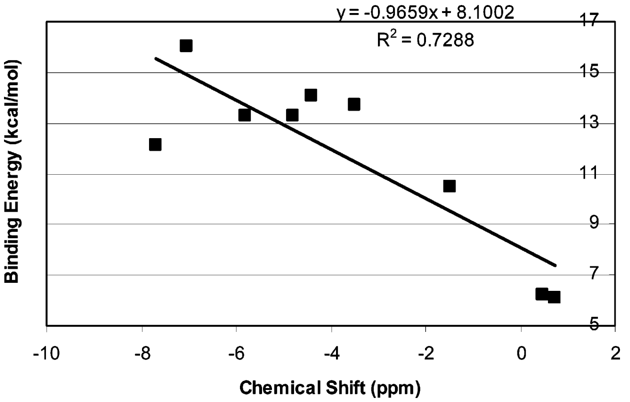


Figure 7. Calculated trialkylborane−amine binding energies for catalysts vs NMR measured boron chemical shift for trialkylborane−amine catalysts.

of less than about 11 kcal/mol, a ^{11}B anion chemical shift more positive than −2 ppm, or a DSC determined decomposition temperature less than 50 °C have a significant probability of being unstable, and potentially hazardous even at high amine-to-trialkylborane ratios. In some cases (i.e., pyrrolidine), the trialkylborane was an effective adhesive catalyst and adhesion promoter, was not pyrophoric, and had an exothermic decomplexation observed by DSC, but was not detected by thermoviscometry. In these cases it seems possible that the free amine is interfering with radical production or propagation in the experiment. In the adhesive formulation the amine is complexed by the acid and cannot interfere this way.

Conclusion

Trialkylboranes are increasingly employed as low-temperature catalysts for radical chemistry initiation. This article has shown that amine complexes of trialkylboranes can block oxidation, that subsequent radical generation takes place, and that the stabilization is a function of the bond energy of the B−N bond formed. This bond energy can be probed by numerous direct and indirect methods including ^{11}B NMR, DSC, ab initio calculation, and by thermoviscometry of catalyzed monomer. The correlations of predicted stability among these techniques is imperfect but generally consistent.

Acknowledgment. We would like to acknowledge Dr. Ray Drumright for a thorough review of this article, the assistance of Mr. Daniel Harrington in some of these experiments, and the Dow Chemical Co. for its support of this research.

Supporting Information Available: Tables of additional DSC data and figures showing ^{11}B NMR data, DSC data, enthalpies of reaction, and graphs of structure property relationships. 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) Rahut, H. W. *Adhes. Age* **1969**,*12*, 28−38.
(3) Devine, A. T.; Bodnar, M. J. *Adhes. Age* **1969**, *12*, 35−37.
(4) Clemens, R. J.; et al. *Prog. Org. Coat.* **1994**, *24*, 43−54.
(5) Badey, J. P.; et al. *Int. J. Adhes. Adhes.* **1996**, *16*, 173−178.
(6) Schonhorn, H.; Hansen, R. H. *J. Appl. Polym. Sci.* **1967**, *11*, 1461−1474.
(7) Westerdahl, C. W.; Hall, J. R.; Schramm, E. C.; Levi, D. W. *J. Colloid Interface Sci.* **1974**, *47*, 610−620.
(8) Blais, P.; Carlsson, D. J.; Csullog, G. W.; Wiles, D. M. *J. Colloid Interface Sci.* **1974**, *47*, 636−649.
(9) Schmitz, P. J.; Holubka, J. W. *J. Adhes.* **1995**, *48*, 137−148.
(10) Brewis, D. M. Mathiewson, I.; Wolfsenberger, M. *Int. J. Adhes. Adhes.* **1995**, *15*, 87−90.
(11) Yang, J.; Garton, A. *J. Appl. Polym. Sci.* **1993**, *48*, 359−370.
(12) (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.; U.S. Patent 6,762,260, 2004. (f) Sonnenschein, M. F.; Wendt, B. L. PCT WO 2005/082912 A1, 2005.
(13) Skoultchi, M. M.; Merlo, N. V. U.S. Patent 5,106,928, 1992.
(14) (a) Zharov, J. V.; Krasno, J. N. U.S. Patent 5,539,070, 1996. (b) Deviny, E. J. U.S. Patent 5,990,036, 1999. (c) Pocius, A. U.S. Patent 6,093,778, 2000.
(15) Maandi, E. U.S. Patent 6,632,908, 2003.
(16) Kendall, J. L. Righettini, R. F.; Abbey, K. J. U.S. Patent 6,646,076, 2004.
(17) Diakoumakos, C. D. Kotzev, D. L. PCT. WO 2005/044867 A1, 2005.
(18) Chung, T. C.; Jiang, G. J.; Rhubright, D. *Macromolecules* **1993**, *26*, 3467−3471.
(19) Wang, Z. M.; Hong, H.; Chung, T. C. *Macromolecules* **2005**, *38*, 8966−8970.
(20) Ingold, K. U. In *Free Radicals*; Kochi, J., Ed.; Wiley: New York, 1973; Vol. 1, p 80.
(21) Sonnenschein, M. F.; Webb, S. P.; Kastl, P. K.; Arriola, D. J. Wendt, B. L.; Harrington, D. R.; Rondan, N. G. *Macromolecules* **2004**, *37*, 7974−7978.
(22) Muetterties, E. J. *The Chemistry of Boron and its Derivatives*; Wiley: New York, 1967.
(23) Hoberg, H.; Gotz, V. *J. Organomet. Chem.* **1976**, *118*, C3−C5.
(24) Welch, F. J. *J. Polym. Sci.* **1962**, *61*, 243−252.
(25) Johnson, R. M.; Siddiqi, I. W. *The Determination of Organic Peroxides*; Pergamon Press: Oxford, U.K., 1970.
(26) Pocius, A. V. *Adhesion and Adhesives Technology*; Hanser, Munich, Germany, 1997 pp 42−45.
(27) Spartan 2004 Wavefunction Inc.: Irvine, CA.
(28) The reliability of these calculations is illustrated by comparing the calculated the dissociation energy of diethylperoxide 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.
(29) Cox, S. R.; Williams, D. E. *J. Comput. Chem.* **1981**, *2*, 304−323.
(30) Johnson, J. R.; Snyder, H. R.; Van Campen, M. G. *J. Am. Chem. Soc.* **1938**, *60*, 115−121.
(31) Peerboom, R. A.; Ingmann, S.; Nibbering, N. M.; Liebman, J. F. *J. Chem. Soc., Perkin Trans.* 2 **1990**, 1825−1827.
(32) Gonzalez, A. I.; et al. *J. Phys. Chem.* **1996**, *100*, 10490−10496.
(33) Alder, R. W. *Chem. Rev.* **1989**, *89*, 1215−1223.
(34) Spiegel, D. A.; Wiberg, K. B.; Schacherer, L. N.; Medeiros, M. R.; Wood, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 12513−12515.
(35) Nöth, H.; Wrackmeyer, B. *Chem. Ber.* **1974**, *107*, 3070−3088.
(36) House, H. O. *Modern Synthetic Reactions*; Benjamin Cummings: Menlo Park, CA, 1972.
(37) Herrington, R.; Nafziger, L.; Hock, K.; Moore, R.; Casati, F.; Lidy, W. In *Flexible Polyurethane Foams*; Herrington, R., Ed.; Dow Chemical: Midland, MI, 1997; pp 2−32.

MA060268W