Remote Polymerization of Coatings with the Release of Borane from Its Amine Complex

Andrei V. Fedorov,[1] Andrey A. Ermoshkin,[2] Douglas C. Neckers[2]

[1]*Wright Photoscience Laboratory, Bowling Green State University, Bowling Green, Ohio 43403*
[2]*Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403*

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ABSTRACT: We define *remote polymerization* as the formation of a photopolymer without the benefit of either light or a photoinitiator. In the reported experiments, a radical-generating trialkylborane–oxygen system was used with an active trialkylborane that was released from its stable amine complex by a vaporous (i.e., gas-phase) reagent. Acrylates and methacrylates were polymerized after oxidative radical formation from the highly reactive borane. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 147–152, 2008

Key words: coatings; curing of polymers; initiators; radical polymerization

INTRODUCTION

Many industrial coatings use photopolymers produced by processes in which radicals or cations that generate polymeric chains are obtained from susceptible small molecules after the absorption of light quanta. Recent efforts in this laboratory have focused on remote photopolymerization or curing, a concept in which free-radical polymerization is achieved, on demand, at room temperature without the use of light. Two initiating systems responding to H_2O_2 vapor have been previously investigated. Oxalate and glyoxylate esters have efficiently initiated the radical polymerization of acrylates.[1] Tetraalkyl borate salts from which radicals are generated after oxidation are also acceptable sources of polyacrylates.[2] Complexes of organoboranes with amines are the key components of the systems reported herein.

Organoboranes are well-documented, oxygen-susceptible, free-radical initiators.[3–7] Trialkylboranes are difficult to handle because they are very reactive, even pyrophoric, and borane stabilization has long been achieved through complexation with amines or ethers. Amine–borane complexes, when treated with Lewis acids, form the basis for several commercial two-part adhesive formulations, including those displaying improved adhesion to low-energy surfaces.[8–29]

The remote activation of systems investigated herein results from an agent that is delivered to a coated surface in a stream of a carrier gas to trigger the release of a trialkylborane from its complex with an amine. The released borane reacts with oxygen-generating alkyl radicals that cause the polymerization of acrylate or meth(acrylate) monomers (Scheme 1). The advantage of this remote curing system is that radicals can be generated in places that light cannot reach, such as the interior of a pipe.

EXPERIMENTAL

Materials

All acrylic/methacrylic monomers and oligomers were obtained from Sartomer (Exton, PA) or UCB Chemicals (Smyrna, GA) and used as received. 4-*N*,*N*-dimethylaminopyridine (4DMAP; 96%) and triethylborane (Et_3B; >95%; Aldrich, Milwaukee, WI) were used without further purification. The sources, purities, boiling points, and vapor pressures of all other agents are listed in Supplementary Table I. Nitrogen, argon, and air (all research-grade) were obtained from Linde.

Trialkylborane complexes with amines were synthesized according to methods described elsewhere.[30] These complexes (Supplementary Tables II–IV) offered a variety of stabilities upon dissolution in formulation, and the addition of a small excess of a free

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Correspondence to: D. C. Neckers (neckers@photo.bgsu.edu).

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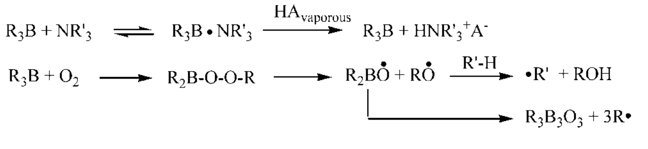

Scheme 1

amine significantly increased their stability (Supplementary Table V). Amine complexes containing multiple nitrogen sites were most effective. Complexes of Et_3B with 4DMAP and hydrazine were mainly used in this work.

In situ measurements of the degree of polymerization

The degree of polymerization was monitored *in situ* with a CM-1000 cure monitor (Spectra Group, Ltd., Milbury, OH). This measured the fluorescence changes induced by changes in the microviscosity in the environment surrounding a small molecular probe in a polymerizing formulation.[31–33] These fluorescence changes reflected photopolymer chain growth and were proportional to the percentage of the double-bond conversion (%DB).[34–35] The fluorescent probe 1-dimethylaminonaphthalene-5-sulfonyl-*n*-butylamide (0.1 wt %), excited at 350 nm with fluorescence intensities monitored at 456 and 558 nm, was used. By monitoring the ratio of the fluorescence intensities at two different wavelengths, we could eliminate artifacts.[36,37]

Measurements of the double-bond conversion on the surface of the cured films

4DMAP (18 mg, 0.15 mmol) was completely dissolved by moderate heating and sonication in dipropylene glycol diacrylate (DPGDA; 6 g, 24.8 mmol). The solution was cooled to room temperature, and this was followed by the addition of 4DMAP·Et_3B (300 mg, 5 wt %, 1.37 mmol) and 120 mg (1.9 wt %) of the surface additive BYK-330. A layer of the formulation of a designated thickness was deposited onto a polyethylene sheet (surface energy = 40–42 dyn/cm to ensure the detachment of the polymer film that formed) with drawdown square gaps.

Saturation with a reactive vapor was achieved by the passage of nitrogen through a bubbler filled with acetic acid maintained at room temperature, and this was followed by a subsequent pass through a trap to prevent the formation of liquid droplets. We allowed 30 s to elapse before filling the 2-L chamber in which polymerization was to occur. No controlled amount of oxygen was introduced into the system; only oxygen that dissolved in the formulation was available to react with the borane released. The polyethylene substrate coated with the formulation was inserted into the chamber for 3 min. After exposure,

TABLE I

Responses to Different Reactive Agents of a Trimethylolpropane Formulation Containing a Complex of Et_3B with Either Hydrazine or 4DMAP

		Et_3B·hydrazine		Et_3B·4DMAP	
Reactive agent	Calculated vapor pressure at 20°C (mmHg)[a]	Film thickness (μm)	%DB	Film thickness (μm)	%DB
Formic acid (HCOOH; $pK_a = 3.75$)	28	80	77	120	68
Acetic acid (CH_3COOH; $pK_a = 4.75$)	16	120	82	81	35
Propionic acid (C_2H_5COOH; $pK_a = 4.86$)	5.4	85	35	70	38
Acrylic acid ($CH_2{=}CHCOOH$; $pK_a = 4.25$)	2.4	6	64	46	59
Hydrochloric acid (HCl)	N/A	18	6.5	33	71
Acetic anhydride [$(CH_3CO)_2O$]	4.4	71	78	—[c]	—[b]
Boron tribromide (BBr_3)	48	3	—[b]	4	—[b]
Silicon tetrachloride ($SiCl_4$)	188	10	37	95	65
Tin tetrachloride ($SnCl_4$)	18	135	67	16	—[b]
Oxalyl chloride $(COCl)_2$	137	127	65	148	74
Acetyl chloride (CH_3COCl)	242	54	69	73	62
Benzoyl chloride (PhCOCl)	0.27	8	—[b]	9	—[b]
ortho-Chlorophenol (*o*-ClC_6H_4OH)	0.6	—[c]	—	N/A	N/A
Acetone (CH_3COCH_3)	197	—[c]	—	N/A	N/A
Acetic aldehyde (CH_3CHO)	746	380	76	N/A	N/A
Toluene 2,4-diisocyanate at 20°C	0.01	—[c]	—	N/A	N/A
Toluene 2,4-diisocyanate at 100°C	3.85	35	54	N/A	N/A
Sulfur dioxide (SO_2)	—	117	74	N/A	N/A

N/A = not applicable.

[a] Calculated with the ChemCraft suite of programs.

[b] The near-IR spectrum of the film was not suitable for the determination of the ratio between the aliphatic and olefinic hydrogens.

[c] No film formation occurred, or a very thin gel-like film not suitable for future investigation was obtained.

TABLE II
Stability and Response to CH_3COOH Vapor for Formulations Containing Commonly Used Acrylic and Methacrylic Monomers and $Et_3B\cdot 4DMAP$[a,b]

Monomer	Viscosity (cP)	Density (g/mL)	Stability after 12 h (%DB)	Film thickness (μm)	%DB
Acrylate					
2-(2-ethoxyethoxy) ethyl acrylate	6	1.013	0	—[c]	86
1,6-Hexanediol diacrylate	9	1.020	3	240	34
Dipropylene glycol diacrylate	10	1.052	0	150	89
Trimethylolpropane triacrylate	106	1.109	0	81	35
Ethoxylated pentaerythritol tetraacrylate	—	1.128	0	34	64
Methacrylate					
Isobornyl methacrylate	10	0.979	—	—[c]	68
Neopentyl glycol dimethacrylate	8	1.000	4	359	34
Trimethylolpropane trimethacrylate	44	1.061	—	130	26

[a] The formulation contained the monomer and 5 wt % Et_3B complex with 4DMAP.

[b] The humidity was 45%, the temperature was 25°C, and ambient light was used.

[c] The entire volume of the monomer was polymerized for 30 min after the formulation exposure.

the now coated substrate was removed from the chamber, and the top surface was washed with acetone and dried. The resulting polymer film was detached from the substrate and used for %DB measurements.

Fourier transform infrared (FTIR) spectra of liquid formulations (unpolymerized) and polymer films were measured with a Shimadzu 8400 FTIR spectrometer equipped with a Pike Technology attenuated total reflection accessory (Columbia, MD). Attenuated total reflection FTIR spectra of the films were taken for both the exposed (top) and unexposed (bottom) sides. %DB was determined by the monitoring of the acrylic wag peak at 809 cm^{-1}, which was internally referenced to the C=O fundamental. %DB was compared for both the top and bottom surfaces to evaluate the depth of the cure.

Formulations

The formulations for remote cure screening (Tables I–V) contained 5 wt % borane–amine complex dissolved in 1.5 g of an acrylic resin. Polymer films were obtained after 2 min of exposure of a 2-mm-thick layer of the formulation (area of the bottom of the glass vial = 0.79 in.^{2}) to the flow of a vapor of

TABLE III
Thickness of the Films for Remotely Cured Model Acrylic Formulations[a]

Model formulations for different substrates	Excess amine [mass % (mol) %][b]	Formulation stability after 1 h[c]		Film thickness (μm)[d]
		20°C	60°C	
Wood (54.3% urethane acrylate oligomers and 46.7% acrylic diluents)	0 (0)	+	−	79
	5.54 (10)	+	±	90
	11.08 (20)	+	+	71
	27.74 (50)	+	+	41
Polycarbonate (45.2% urethane acrylate oligomers, 55.8% acrylic diluents, and 2.0% silicone surface additive)	0 (0)	+	−	115
	11.08 (20)	+	+	92
	27.74 (50)	+	+	86
Glass (50% acrylated aliphatic urethane and 50% acrylic diluents)	27.74 (50)	+	−	57
	111 (200)	+	+	38
Aluminum (36.9% acrylated epoxy resin, 34.3% multifunctional acrylate, and 28.8% acrylic diluents)	111 (200)	+	+	115
Tile (70% acrylated aliphatic urethane, 15% multifunctional acrylate, and 15% acrylic diluent)	0 (0)	+	−	110
	5.54 (10)	+	+	102
Metal (proprietary formulation)	0 (0)	+	−	107
	55.5 (100)	+	+	83

[a] The coating formulations contained 5 wt % $Et_3B\cdot DMAP$. The free amine that was added was 4DMAP. The reactive agent was formic acid vapor.

[b] The concentration of excess amine was based on the amount of a borane amine complex.

[c] The following criteria were used: + = stable, ± = marginally stable, and − = unstable. A formulation was considered stable if no visible signs of gelation and/or polymerization occurred in a designated time under specified conditions.

[d] Before exposure to the release agent, all formulations were stored at 20°C for 1 h.

TABLE IV
Thickness of the Films Prepared from Formulations Cured by Vapors of a Borane–Amine Complex[a]

Complex	HCOOH (wt %)	Film thickness (µm)
$Et_3B{\cdot}H_2NNH_2$	0	—
maintained at 60°C	5	50
	10	35
	20	11
$Et_3B{\cdot}H_2NNH_2$	0	—
maintained at 100°C	5	38
	10	6
	20	20
$Et_3B{\cdot}H_2N{-}CH(CH_3)_2$	0	—
maintained at 25°C	5	5
	10	4
	20	5

[a] The formulation contained trimethylolpropane triacrylate and formic acid.

the reactive decomplexing agent delivered in a stream of argon (gas line diameter = ¼ in.). The thickness of the resultant polymer film was measured with a micrometer. %DB was determined by near-IR spectroscopy.[38,39] Control experiments in which formulations containing no borane–amine complex were exposed to the reactive agent vapor yielded no polymerization.

RESULTS AND DISCUSSION

The DPGDA monomer containing $Et_3B{\cdot}4DMAP$ (Fig. 1) showed no detectable conversion of double bonds before exposure to acetic acid vapor. Polymerization was achieved after the introduction of acetic acid vapor, and the rate of polymerization increased as the $Et_3B{\cdot}4DMAP$ concentration in the formulation was increased. In the case of the largest load (5%), polymerization was complete in less than 2 min. Our trials showed good reproducibility (Fig. 1, inset).

Complexes of borane with an amine are formed by a Lewis acid–base reaction (Scheme 1), with the stability and reactivity of the complex depending on the basicity of the amine. More basic amines form more stable complexes (Supplementary Tables II–IV). We found it practical to stabilize formulations containing borane–amine complexes through the addition of a small amount of the free amine (Supplementary Table V). The addition of a Lewis acid that is a stronger acid than borane results in the dissociation of the complex and the release of free borane (Scheme 1).

TABLE V
Effect of the Carrier Gas on the Remote Cure[a]

Carrier gas	Film thickness (µm)	%DB
Argon	104	72
Nitrogen	91	62
Air	88	48

[a] The formulation contained trimethylolpropane triacrylate and 5 wt % $Et_3B{\cdot}DMAP$ complex.

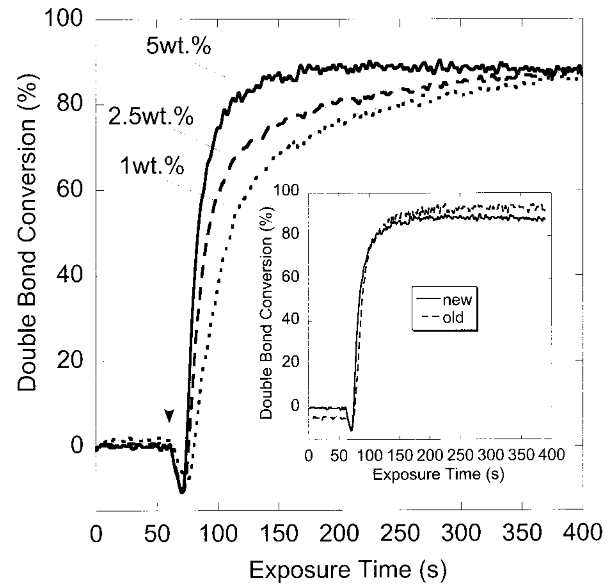

Figure 1 Polymerization kinetics obtained for DPGDA containing various amounts of the complex of Et_3B with 4DMAP. The time of activation by acetic acid vapor is indicated by an arrow. The thickness of the polymerized layer was 100 µm. Inset: polymerization kinetics obtained for (—) freshly prepared and (- - -) 2-week-old formulations containing 5 wt % of the complex.

The novelty of the polymerization method described herein is in delivering the reactive reagent in the vapor phase. Because the efficiency of the polymerization depends on the penetration of the reactive agent, we investigated the depth of the cure by comparing %DB for the exposed and unexposed surfaces of films of various thicknesses (Fig. 2). Although %DB at the exposed surface remained essentially constant within the experimental error, a gradual decrease in %DB at the unexposed surface was observed as the film thickness increased. For relatively thin layers, the diffusion of a reactive agent (i.e., acetic acid) into the film was sufficient to ensure a complete and thorough cure. As the layer thickness increased, the vaporous reactive agent delivered from the top could not efficiently penetrate the entire depth of the coated layer. This resulted in undercuring of an unexposed bottom surface. The results for DPGDA cured by acetic acid vapor indicated an acceptable, thorough cure in layers up to 100 µm (4 mil) thick.

Different groups of vaporous activating agents that interacted with amines were examined (Table I). The observed film thickness and degree of double-bond conversion were influenced by a combination of factors. Both the volatility of the activating agent

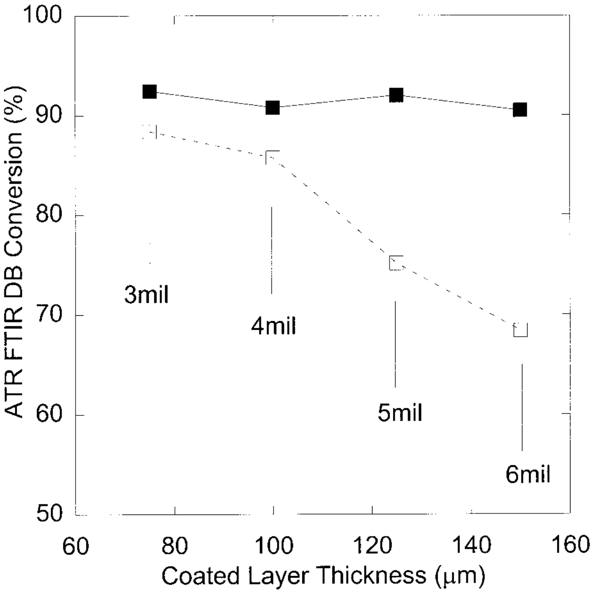

Figure 2 %DB as a function of polymer film thickness at the surface of the formulation (DPGDA containing 5 wt % of the complex of trialkylborane with 4DMAP): (■) exposed for 3 min to a vapor of acetic acid and (□) unexposed.

and its affinity for the complexed amine were important. These multiple factors masked clear identification of trends in the reactivity for different activating agents.

More volatile agents were more reactive because of the higher concentration of the vaporous activating agent in the stream of the carrier gas. Agents with a higher affinity for the complexed amine resulted in faster and more efficient release of trialkylborane. This led to a higher degree of double-bond conversion but could also result in thinner films because the faster cure prevented deep penetration of the activating agent.

All the strong carboxylic acids were efficient activating agents for both the hydrazine and 4DMAP complexes of Et_3B (Table I). Volatile acid chlorides were also very reactive for both of the complexes examined. Lewis acids yielded different results. $SiCl_4$ was more efficient for the 4DMAP complex, whereas $SnCl_4$ displayed higher reactivity with Et_3B·hydrazine. Boron tribromide displayed no significant reactivity. This indicated that boron tribromide had a lower affinity for the amines in comparison with complexed Et_3B.

Toluene 2,4-diisocyanate became active only when sufficient vapor pressure was achieved by an increase in the temperature in the bubbler from 20 to 100°C. Some agents liberated the borane from its complex with a particular amine but were inactive with other complexes. For example, acetaldehyde selectively released Et_3B from its complex with hydrazine. Both 2-chlorophenol and acetone had a very low affinity for amines, so these evidenced no reactivity.

We examined the cure response for several monofunctional and multifunctional acrylic monomers (Table II). Thinner polymer films were obtained for more viscous monomers. This could be explained by less efficient penetration of the reactive vapor into higher viscosity monomers on the basis of the inverse proportionality between the coefficient of diffusion and the viscosity of the medium.[40] As discussed previously, the viscosity increase caused by the growing polymer chains also enforced limitations on both the depth and degree of remote polymerization. The slower polymerization rates of the methacrylates resulted in deeper penetration of the reactive agent. Accordingly, the methacrylates yielded thicker films and lower %DB values than the acrylates.

We used formic acid vapor to remotely cure several acrylic resins on different substrates (Table III). The viscosity of model resins is generally higher than that of acrylic and methacrylic monomers, so the resins are often processed at elevated temperatures. Acrylated urethane and acrylated epoxy oligomers in resin formulations might also contain minor amounts of species capable of releasing borane, such as unreacted diisocyanates and acids. Therefore, the stability of the complexes in the formulations was evaluated at both 20 and 60°C. When stability was not achieved, additional amounts of amine were introduced to stabilize the complex by shifting the complexation equilibrium (Scheme 1).

The formation of a polymer film upon exposure to formic acid vapor was observed for all resins examined (Table III). The presence of excess amine resulted in thinner films, which were indicative of less efficient curing. This occurred because the activating agent consumed the more reactive uncomplexed amine before interacting with the borane–amine complex.

The roles of the reactive agent and borane–amine complex could be reversed. The reactive agent could be dissolved in the resin with the polymerization remotely activated by a volatile borane–amine complex delivered in a stream of a carrier gas (Table IV). Thus, we successfully initiated radical polymerization with Et_3B·hydrazine vapor and a trimethylolpropane triacrylate formulation containing formic acid.

The vapor of uncomplexed Et_3B was also effective, and several monomers were successfully polymerized (Supplementary Table VI). However, various difficulties arose in the handling of the system because Et_3B is pyrophoric.

The polymerization results also depended on the carrier gas type (Table V). Argon was the best carrier and was followed by nitrogen. A somewhat less efficient polymerization was observed in air because of an inhibition of radical polymerization by excess oxygen.

CONCLUSIONS

We have developed an efficient remote polymerization method for acrylates and methacrylates using the interaction between complexes of trialkylborane with an amine and reactive acid vapor. The efficiency of the system has been tested with different acrylic formulations. This technology has potential for industrial applications.

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