

Ambient Polymerization of Acrylic Pressure Sensitive Adhesives

Timothy Mitchell, Industry Specialist, Dow Corning Corporation, Midland, Mi
Dongchan Ahn, Senior Research Specialist, Dow Corning Corporation, Midland, Mi

Introduction

Traditional solution acrylic polymers for pressure sensitive adhesives (PSA) are synthesized using conventional free radical initiation systems based upon organic peroxide or azo compounds¹. Such syntheses are heat activated and employ solvent reflux temperatures during the polymerization process. The resulting acrylic polymers are formed with a relatively broad molecular weight distribution which can diminish both the processing and adhesive performance of the final product. To overcome this limitation, a variety of controlled radical polymerization (CRP) methods have been developed to synthesize acrylic polymers with controlled architectures including nitroxide-mediated CRP (NM-CRP), atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer polymerization (RAFT)²⁻³. These techniques provide control of molecular weight and can produce polymers with narrow molecular weight distributions. However, these techniques can be expensive, require long preparation times, use heavy metal catalysts and/or have significant odor. For applications such as PSAs where high structural precision is helpful not essential, the additional processing costs render CRP difficult to justify over conventional polymerization schemes. Using a novel polymerization initiator system, it is now possible to synthesize acrylic polymers with controlled molecular weights of unexpectedly narrow distributions in facile ambient atmospheric conditions. These novel acrylic PSAs exhibit improved control of adhesive performance over conventional free radical initiation systems without the processing complications of CRP methods⁴.

Background

Certain organometallic compounds have been shown to act as effective initiators for the free radical polymerization of vinyl monomers at low temperatures in the presence of oxygen or peroxy compounds. Organometallic compounds that are particularly efficient include the group three elements with the organoboranes as the most active of the species⁵⁻⁷. There are several examples in the literature of compositions of acrylic monomers that are capable of being polymerized by an organoborane⁷⁻¹². These publications are largely directed toward two-part, ambient cure-in-place structural adhesive systems that include an organoborane amine complex, an amine reactive compound, or decomplexer, and acrylic monomers that are capable of undergoing free radical polymerization¹³⁻¹⁴. However, these publications do not discuss characterization of the polymerization products for PSA applications.

Organoboranes are reactive with oxygen and most are pyrophoric. The amine serves to stabilize the organoborane in air so that it may be incorporated into a polymerizable system. Depending on the amine and the organoborane, these complexes may be very stable in an ambient environment. An example of such an organoborane-amine complex, tri-n-butylborane methoxypropylamine (TnBB-MOPA) is shown in Figure 1. During application, the decomplexer reacts with the amine rendering the organoborane free to initiate polymerization of the monomers. Suitable amine reactive materials include acids, carboxylic acid-functional materials such as acetic acid or acrylic acid, isocyanates, acid chlorides and anhydrides.

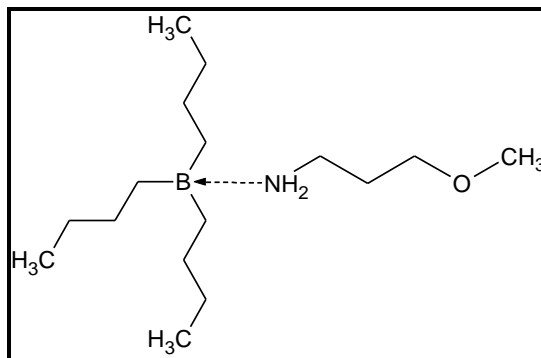
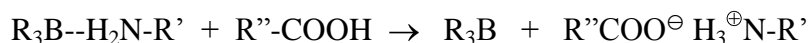


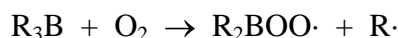
Figure 1: Chemical structure of TnBB-MOPA initiator complex used for the RTA polymerization of acrylic pressure sensitive adhesives.

Descriptively, room temperature alkylborane (RTA) polymerizations occur rapidly in ambient conditions when an alkylborane-amine complex and an amine-reactive compound, or decomplexer, are mixed together to initiate free radicals in the presence of a monomer or mixture of radical polymerizable monomers. Polymerization via alkylborane initiators is most effective with activated double bonds, typically through electron withdrawal of neighboring groups, and acrylate and methacrylate functional materials provide a wide range of relatively inexpensive materials that can readily be polymerized and co-polymerized by this approach. Initiation of the decomplexed alkylborane requires oxygen to form the free radicals, so inert atmospheres are not required for the polymerization reaction as shown in Figure 2.

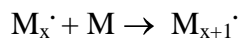
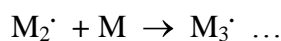
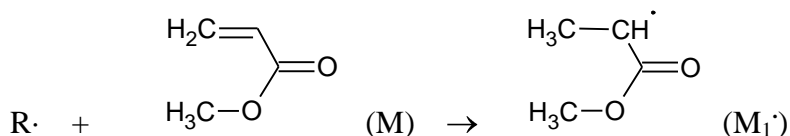
(a) Decomplexation (on mixing)



(b) Initiation (instantaneous in ambient air)



(c) Propagation



(d) Termination (e.g. by combination)



Figure 2: Examples of the key steps in the free radical polymerization of methyl acrylate via room temperature alkylborane (RTA) initiators. These do not represent all the possible reactions and are simply used to illustrate the general processes involved in RTA polymerizations.

Between the minimal air contact of reactants at the liquid surface and the intrinsic oxygen content in monomers and solvents, ambient conditions present very suitable conditions for polymer synthesis in most reactor geometries. There are a number of features that differentiate RTA polymerizations from other methods. The most important is the ability to carry out the chemistry extremely rapidly at ambient conditions with no atmospheric purging. Rather than using heat or UV light to generate free radicals, very stable organoborane-amine complexes are mixed with common amine-reactive compounds to safely and rapidly liberate the organoborane free radical source in the monomer solution to yield acrylic pressure sensitive adhesives.

Results and Discussion

I. Background Experiments

Rapid homopolymerization of an acrylic monomer can be demonstrated with a very simple vial mixing experiment. Figure 3 shows the progression of the polymerization of neat methyl acrylate mixed with TnBB-MOPA at concentration of 3000 ppm elemental B (w/w). Within 5 minutes of introducing the decomplexer, a high viscosity polymer has formed, which resists flow when the vial is inverted (Figure 3 (d)). After 10 minutes, the material exhibits aggressive tack and fibrillation when probed with a metal microspatula (Figure 3 (e)). This behavior is typical of general purpose PSAs.

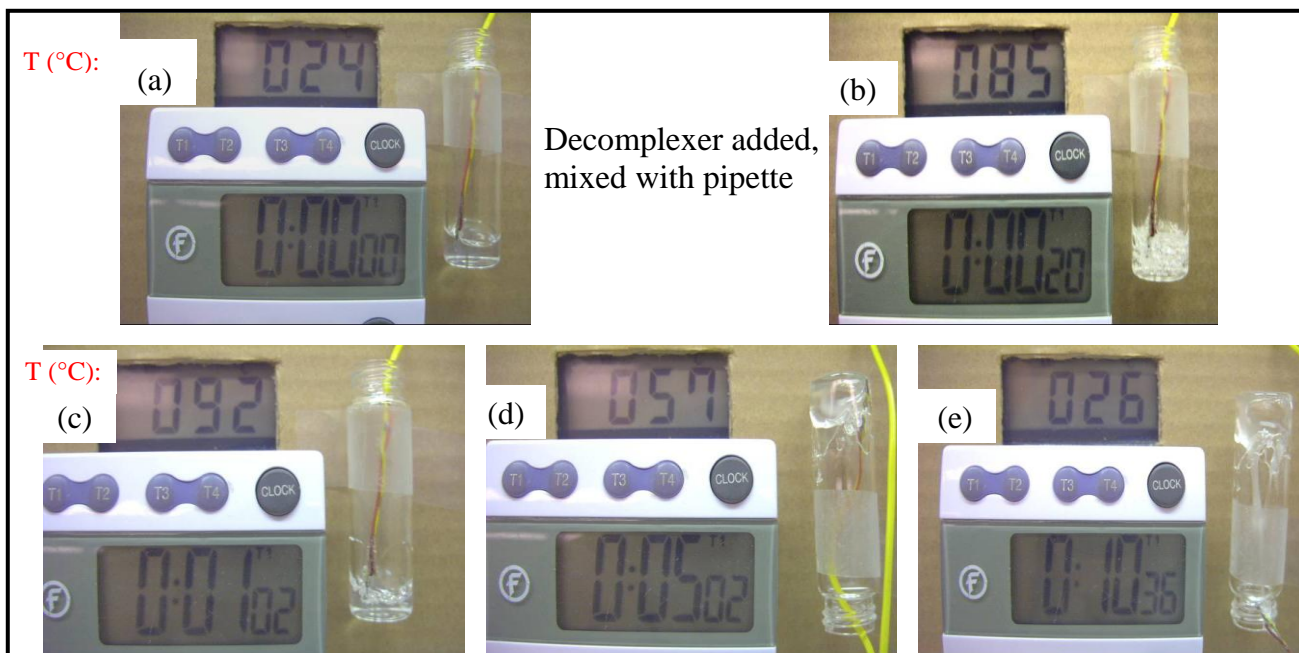


Figure 3: Progression of RTA polymerization of 1 g of methyl acrylate in a glass vial monitored by a thermocouple (output shown on upper display of each figure) and a digital timer for (a) the starting solution of 1 g methyl acrylate mixed with TnBB-MOPA initiator complex at RT, and in (b) – (e) at 20 s, 1 min, 5 min and 10 min, respectively, after introducing isophorone diisocyanate (IPDI) as a decomplexer.

The temperature rise due to heat of polymerization is also significant in this case as seen by a rise of 68°C within 1 minute of mixing even with a relatively small quantity of monomer and large surface area reactor. This behavior merits a reminder of the exothermic nature of bulk acrylate free radical polymerization. When proper measures are not used, bulk polymerizations of low molecular weight monomers can exhibit auto-acceleration, known as the ‘gel effect’ or Trommsdorf effect in the literature¹⁵⁻¹⁷, which can result in potentially dangerous situations, and at the least, a gelled reactor that is difficult to clean. This can be managed by the use of appropriate thermal management techniques, such as dilution, controlled addition rates or cooling systems, to prevent run-away conditions.

RTA polymerizations can also be conveniently monitored by carrying out a small-scale bulk polymerization on an infrared spectrometer equipped with an attenuated total reflectance (ATR) cell. Figure 4 shows the progression of this experiment for the bulk homopolymerization of methyl methacrylate using 2600 ppm B (from triethylborane propanediamine / TEB-PDA) decomplexed by two equivalents of dodecenylsuccinic anhydride, where conversion is tracked by monitoring the disappearance of the polymerizable double bond by tracking peak height of the =CH₂ rocking vibration at 1323 cm⁻¹.¹⁸ Within 5 minutes of mixing, the double bond peak intensity decays by over 80% of the original absorption, reflecting the extent of polymerization.

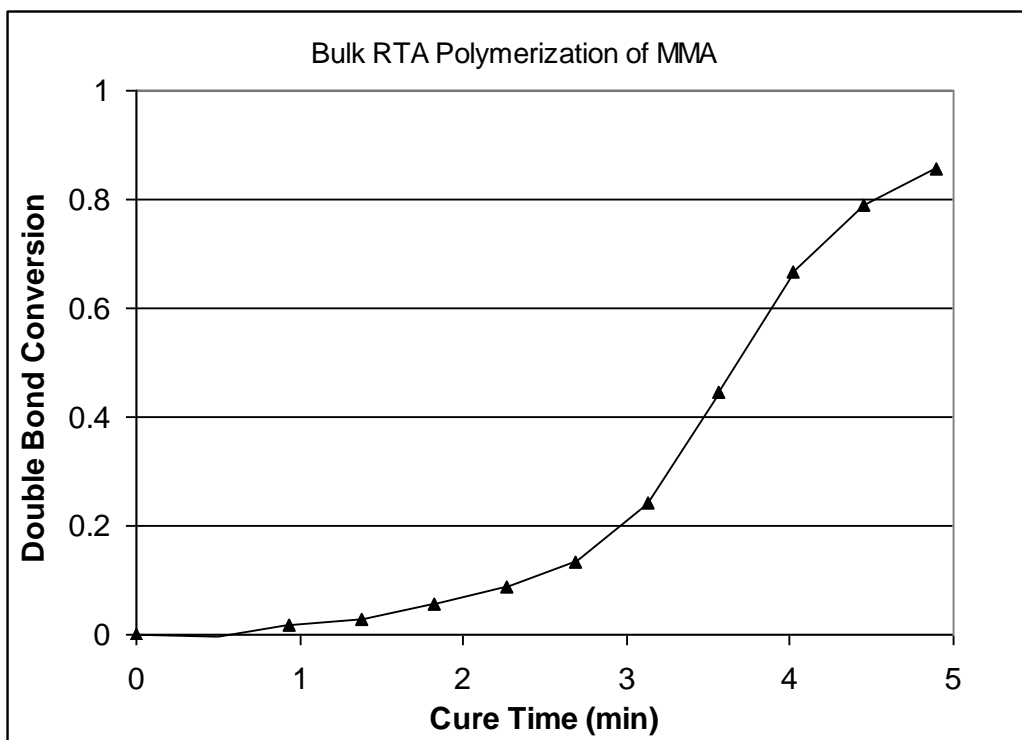


Figure 4: Conversion of MMA into PMMA in an RTA bulk polymerization as monitored by the disappearance of =CH₂ rocking vibration (1323 cm⁻¹) via ATR-IR. Initiator was TEB-PDA (2500 ppm B) decomplexed with two equivalents of dodecyl succinic anhydride. A line is drawn to guide the eye.

Soxhlet extraction studies showed that the polymerization products were fully soluble in THF, confirming that the polymerization was predominantly linear with no significant crosslinking. The products were analyzed by GPC and show surprisingly narrow polydispersity indices at relatively low B loadings. Figure 5 shows the GPC chromatogram in THF using polystyrene standards of an unwashed MMA polymerization carried out with 500 ppm B. The higher MW peak centered on the elution time of roughly 14 minutes corresponds to $M_n = 18,800$, $M_w = 61,700$, yielding a polydispersity index (PDI) of 1.97. Interestingly, this corresponds very well to the theoretical most probable distribution of $PDI = 2.0$ for a free radical polymerization in which the primary mechanism of termination is recombination¹⁹⁻²⁰.

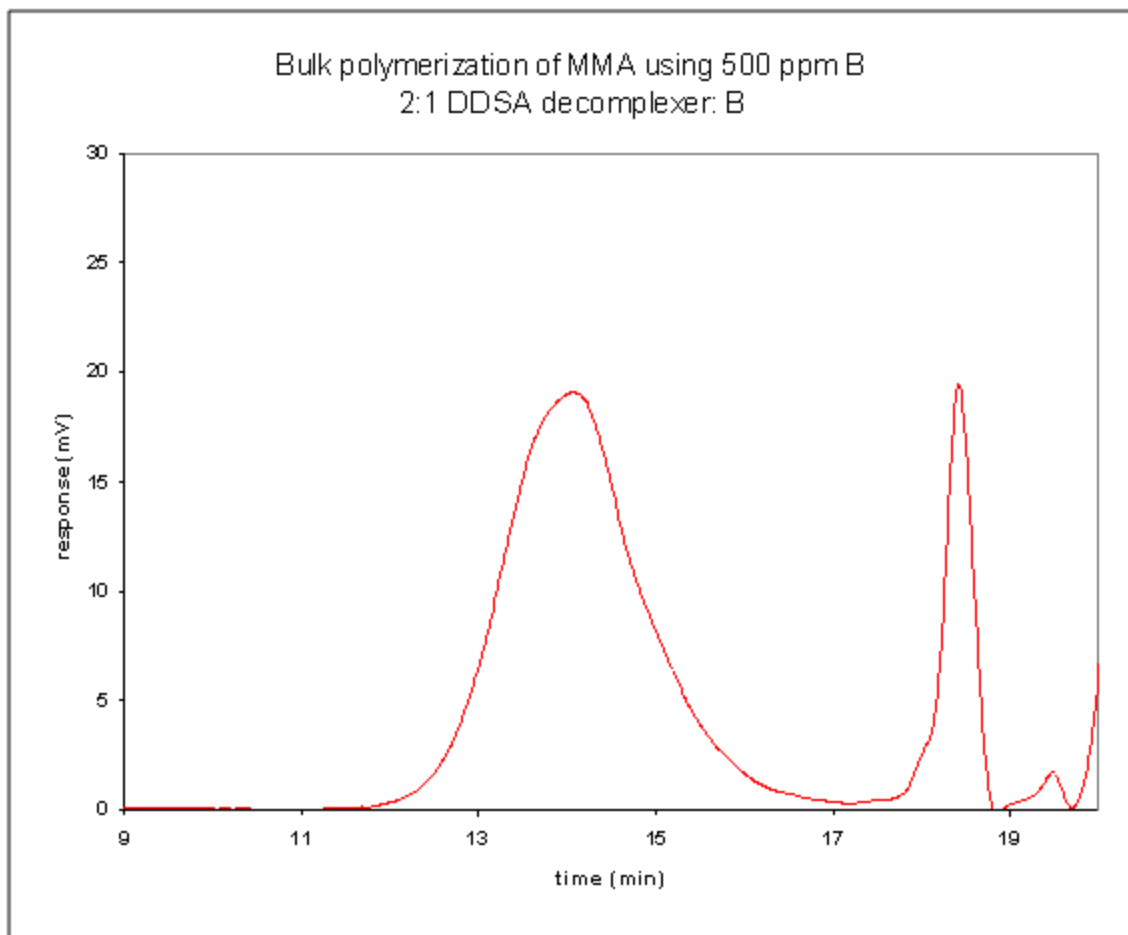


Figure 5: GPC chromatogram of product of MMA polymerized with 500 ppm B under otherwise similar conditions to those used in Figure 4.

These results, using a remarkably simple process of mixing two fluids in ambient conditions with no atmospheric control, motivated the subsequent study of free radical copolymerization to synthesize acrylic pressure sensitive adhesives.

II. Acrylic Pressure Sensitive Adhesives

Two sets of acrylic PSAs were produced using TnBB-MOPA at levels ranging from 500 to 2000 ppm of boron based on monomer concentration. For each set, a control example was polymerized using a traditional free radical initiator (AIBN / Vazo® 64). The AIBN was set at a constant level of 0.06% by weight (0.145 pph based on total monomer level) and the reaction was run at 78°C for 12 hours. In all cases, the control examples use the same monomer compositions as the RTA polymerized examples.

The first series of acrylic PSAs were produced using 2-ethylhexyl acrylate (2-EHA), methyl acrylate (MA) and acrylic acid (AA) at a weight ratio of 70:27:3, respectively. TnBB-MOPA was used at levels of 500, 1000, 1723.8 and 1831.2 ppm B (w/w). The physical properties for the resulting materials are shown in Table 1.

Table 1: Physical property testing results for acrylic PSAs produced using AIBN (Control 1) and TnBB-MOPA with a composition of 70% 2-EHA, 27 % MA and 3% AA.

	Control 1	RTA-1A: 500 ppm B	RTA-1B: 1000 ppm B	RTA-1C: 1723.8 ppm B	RTA-1D: 1831.2 ppm B
Solids (%)	43.7	30.3	35.3	34.9	35.5
Viscosity (cP)	443.1	16700.0	6837.0	2218.0	1909.0
Mn (g/mol)	42,000	264,000	197,000	138,000	130,000
Mw (g/mol)	227,000	812,000	599,000	451,000	415,000
PDI	5.49	3.08	3.04	3.27	3.19
Tg (°C)	-39	-43	-44	-43	-44

Using the solids content as an indicator of polymer conversion, the RTA polymerizations ranged from 72.1 to 84.5% as the concentration of initiator increased. Although the conversion level of RTA-1A was the lowest, the solution viscosity was the highest of all samples. The viscosity of the RTA polymerizations decreased as the level of initiator increased and all were significantly higher than the control sample. The viscosity trend seen in the RTA polymerizations can be directly correlated to the resulting polymer weight properties. As the concentration of initiator increases, the polymer molecular weight decreases. Much like traditional radical polymerizations, the molecular weight properties of an RTA polymerization is a function of initiator concentration. The polydispersity index (PDI) of the polymers synthesized using the RTA system was lower than the control formulation polymerized by AIBN. When using the Fox equation²¹ and the reported Tg for homopolymers²², the predicted Tg for a co-polymer composition of 70% 2-EHA, 27% MA and 3% AA is -37.5°C. The resulting Tg of the control sample was -39°C. The glass transition temperatures obtained for the four samples synthesized by RTA polymerization were consistent and slightly lower than the control sample. Within the set of RTA co-polymers, the Tg of the samples were not statistically different from one another. This indicates that the concentration of initiator does not impact the structure of the resulting co-polymer.

Table 2: Tape performance property testing results for acrylic PSAs produced using AIBN (Control 1) and TnBB-MOPA with a composition of 70% 2-EHA, 27 % MA and 3% AA.

	Control 1	RTA-1A: 500 ppm B	RTA-1B: 1000 ppm B	RTA-1C: 1723.8 ppm B	RTA-1D: 1831.2 ppm B
180 Degree Peel Adhesion - SS (N/10mm)	7.36	4.24	4.54	6.30	6.30
Static Shear - 4psi (minutes)	5.1	193.0	60.4	26.5	17.9
TA - Peak Force (g)	118.78	82.03	91.60	87.74	86.78
TA - Total Area (g.s)	61.99	32.88	54.85	81.30	∞

The tape performance properties obtained for the first series of acrylic PSAs exhibited typical behavior of non-crosslinked acrylic PSAs. The peel adhesion and tack increased while the static shear decreased as the polymer Mw decreased. The control sample had the highest peel adhesion and lowest static shear properties. The peel adhesion of the RTA polymerized PSAs increased as the level of initiator increased. The difference in the level of initiator between RTA-1C and RTA-1D (~100 ppm of boron) was not significant enough to show a difference in the peel adhesion. The static shear testing results for the RTA polymerized PSAs exhibited the expected decreasing trend as the co-polymer Mw decreased. The static shear results for the RTA polymerizations were all higher than the control sample.

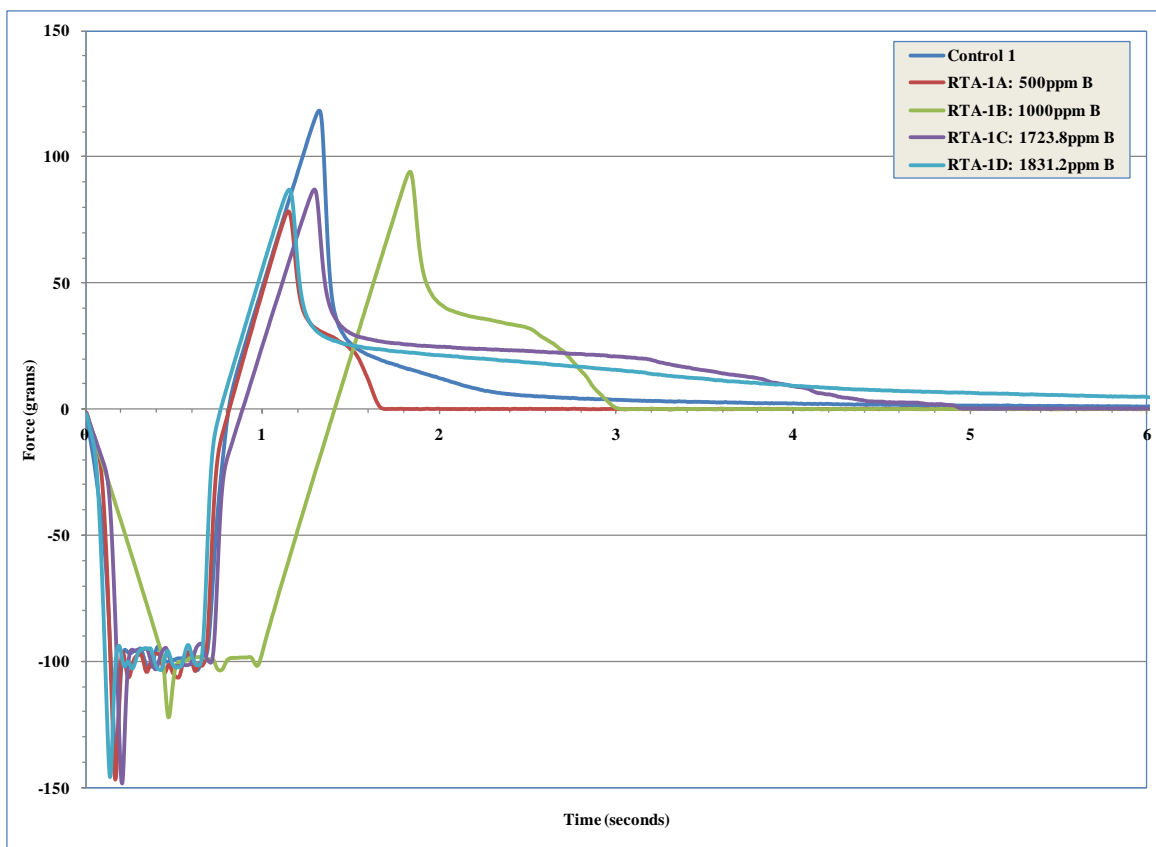


Figure 6: The resulting Texture Analyzer curves for acrylic PSAs produced using AIBN (Control 1) and TnBB-MOPA with a composition of 70% 2-EHA, 27 % MA and 3% AA.

As can be seen in the TA curves, there is a secondary shoulder for each sample which indicates that these PSAs are forming fibrils during the de-bonding step. The secondary shoulder and subsequent distance to probe separation increases as the level of initiator is increased. For sample RTA-1D, the PSA remained attached to the probe at the conclusion of the test. When comparing the RTA polymerized PSAs, it is seen that the Total Area is increasing as the initiator level increases (decreasing polymer Mw) which reflects an increasing trend in tack. The control sample had a high peak force but the total area was between that of RTA-1C and RTA-1D.

The second series of acrylic PSAs were produced using n-butyl acrylate (BA), methyl acrylate (MA) and acrylic acid (AA) at a weight ratio of 73:24:3, respectively. TnBB-MOPA was used at levels of 500, 1000, 1500 and 2000 ppm B (w/w). The physical properties for the resulting materials are shown in Table 3.

Table 3: Physical property testing results for acrylic PSAs produced using AIBN (Control 2) and TnBB-MOPA with a composition of 73% BA, 24 % MA and 3% AA.

	Control 2	RTA-2A: 500 ppm B	RTA-2B: 1000 ppm B	RTA-2C: 1500 ppm B	RTA-2D: 2000 ppm B
Solids (%)	42.8	19.5	31.7	32.3	33.2
Viscosity (cP)	1559.0	2878.0	8537.0	2422.0	1747.0
Mn (g/mol)	73,500	417,000	232,000	163,000	135,000
Mw (g/mol)	359,000	915,000	642,000	462,000	378,000
PDI	4.88	2.19	2.77	2.83	2.81
Tg (°C)	-27	-31	-31	-32	-33

Changing the main monomer from 2-EHA to BA resulted in a decrease in the level of monomer conversion at the lowest RTA initiator loading level. The percent conversion of the RTA polymerizations ranged from 46.4 to 79.0% as the concentration of initiator increased. Aside from RTA-2A, the viscosity of the RTA polymerizations decreased as the level of initiator increased and all were higher than the control sample. The viscosity trend seen in the RTA polymerizations can be directly correlated to the resulting polymer weight properties. The PDI values for this series of co-polymers were lower than the control sample and at a range of 2.19 to 2.83 were comparable to the previous RTA polymerizations. When using the Fox equation, the predicted Tg for a co-polymer composition of 75% BA, 22% MA and 3% AA is -26.8°C. The resulting Tg of the control was -27°C. The glass transition temperatures obtained for the four samples synthesized by the RTA initiator were consistent and slightly lower than the control sample by nearly the same magnitude as the first series. Within this series of RTA co-polymers, the Tg of the samples were not statistically different from one another. This indicates that the concentration of initiator does not impact the structure of the resulting co-polymer and the difference may be simply due to the RTA initiator system.

Table 4: Tape performance property testing results for acrylic PSAs produced using AIBN (Control 2) and TnBB-MOPA with a composition of 73% BA, 24 % MA and 3% AA.

	Control 2	RTA-2A: 500 ppm B	RTA-2B: 1000 ppm B	RTA-2C: 1500 ppm B	RTA-2D: 2000 ppm B
180 Degree Peel Adhesion - SS (N/10mm)	6.28	0.79	2.26	2.50	4.21
Static Shear - 4psi (minutes)	40.1	2392.2	622.7	212.9	77.3
TA - Peak Force (g)	93.63	63.25	76.56	90.20	82.69
TA - Total Area (g.s)	∞	16.03	21.40	24.25	∞

The tape performance properties obtained for the second series of acrylic PSAs exhibited typical behavior of non-crosslinked acrylic PSAs. The peel adhesion and tack increased while the static shear decreased as the polymer Mw decreased. The control sample had the highest peel adhesion and lowest static shear properties. The peel adhesion of the RTA polymerized PSAs increased as the level of initiator increased. When comparing the results of the first series with the second, it was found that changing the main monomer from 2-EHA to BA resulted in lower peel adhesion at comparable initiator loadings. The static shear testing results for the RTA polymerized PSAs exhibited the expected decreasing trend as the co-polymer Mw decreased. The static shear results for the RTA polymerizations were all higher than the control sample. The change to the higher Tg BA main monomer for the second series had the largest impact on the static shear results. When compared at equal initiator loading levels, the static shear for the second series is an order of magnitude higher than in the first series.

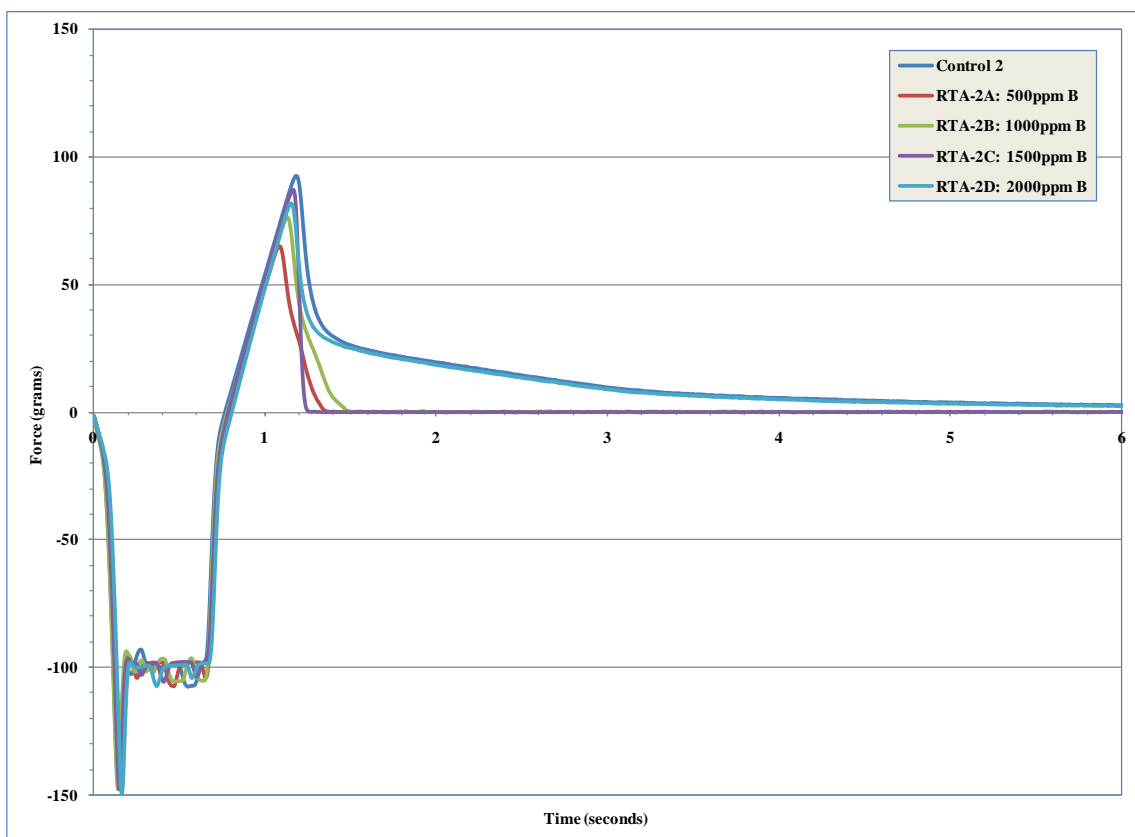


Figure 7: The resulting Texture Analyzer curves for acrylic PSAs produced using AIBN (Control 2) and TnBB-MOPA with a composition of 73% BA, 24 % MA and 3% AA.

As can be seen in the TA curves, the secondary shoulder that had been seen in the previous series has diminished in many samples. There is only a tailing effect seen with RTA-2D and the control. The inclusion of the BA in the second series reduces the effective tack of the PSA compositions when compared to materials made with 2-EHA. When comparing the RTA polymerized PSAs, it is seen that the Total Area is increasing as the initiator level increases (decreasing polymer Mw) which reflects an increasing trend in tack albeit small. The control sample had a high peak force and a total area similar to RTA-2D.

III. Boron Level vs. Polymer Molecular Weight

The RTA polymerizations yielded unimodal GPC elution curves that had narrower molecular weight distributions than what was obtained with AIBN initiated polymerizations of the same composition. The DSC scans of the resulting polymers showed a single intermediate Tg, indicating that random copolymers were formed by this method of addition when the monomers were all pre-mixed. Using the molecular weights measured by GPC, a relationship can be shown between the levels of Boron (initiator concentration) in each sample versus the resulting copolymer molecular weight (Figure 8). Each adhesive, depending on the monomers, solvents, catalyst levels, etc. will have a slightly different curve. However, it is encouraging to observe that in all cases, the molecular weight is an inverse monotonic function of initiator loading. These curves indicate that molecular weight (and hence performance) can be reasonably well predicted by controlling the loading of RTA initiator for a particular monomer mixture.

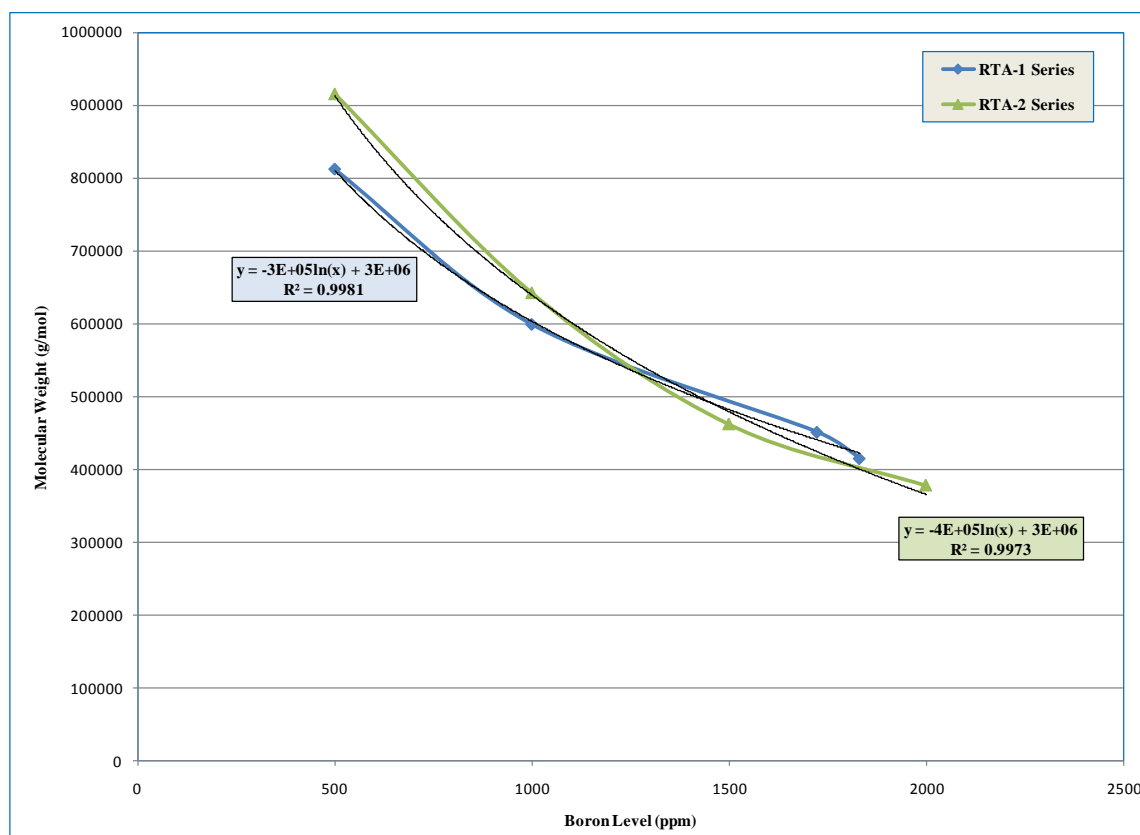


Figure 8: Polymer molecular weight of the RTA polymerized acrylic PSAs as determined by GPC.

Conclusion

This study has demonstrated the feasibility and advantages of using organoborane chemistry to co-polymerize acrylic monomers into model pressure sensitive adhesives. In addition to the process simplification made possible by an ambient process that requires no purging, the resulting co-polymers showed higher average molecular weights and narrower polydispersity indices relative to analogous formulations polymerized by the conventional AIBN-initiated free radical polymerizations. In all cases, a smooth, monotonic inverse relationship between initiator level and number average molecular weight was obtained. This suggests the potential for improved control of the molecular weight and resulting properties of an acrylic PSA.

Experimental

All raw materials for this study were used as obtained from various commercial suppliers.

RTA Polymerization Procedure – Example: RTA-1A

To a 16-ounce glass jar, 50.74 g of 2-EHA, 19.57 g of MA, 2.17 g of AA and 92.37 g of ethyl acetate were added. A lid was secured on the jar and the samples were mixed for a few seconds by hand shaking. Next, 10.15 g of the catalyst (10 wt% TnBB-MOPA in ethyl acetate) was added to the sample jar. The jar was closed and shaken for a few seconds. An exotherm was immediately noticed by the sample becoming warm to the touch. The samples were allowed to mix for 24 hours on a mixing wheel.

Control Polymerization Procedure – Example: Control 1

To a 16-ounce glass jar, 176.49 g of 2-EHA, 68.12 g of MA, 7.59 g of AA and 0.367 g AIBN were added to form a pre-reaction mixture. The materials in this pre-reaction mixture were allowed to stir 15 minutes until thoroughly homogeneous. While mixing, 350.50 g of ethyl acetate solvent was added to a 4-neck glass reactor equipped with a heating mantle, stirring blade/shaft, nitrogen purge, condenser with cooling water and a thermocouple. The pre-reaction mixture was added to a separate pear-shaped glass reservoir. Heating and mixing was then begun on the solvent in the reactor. The reaction temperature was set at 78°C. As soon as the reaction temperature was achieved, the pre-reaction mixture in the reservoir was added at a rate of 0.80 grams/minutes for 320 minutes using a metering pump until the mixture in the reservoir was depleted. The mixture in the reactor was then reacted at 78°C for an additional 1120 minutes to form the acrylate PSA composition. Upon completion, the composition was allowed to cool to room temperature before removing the composition from the reactor.

Solution Viscosity Test Procedure

The viscosity of each sample was determined at 25°C with a Brookfield® DV-II+ viscometer using spindle #5. The viscosities were measured at the fastest RPM the viscometer could handle for the given sample to yield the most accurate reading. All sample sets were measured between 1.5 and 60 RPM's.

Laminate Preparation for Performance Property Testing

PSA laminates were prepared by casting the solvated adhesives onto 2-mil or 10-mil thick polyester (PET) films using a vacuum coating table with an appropriate application bar to yield a 1.0-mil dry PSA thickness. The laminate was placed in an air-circulating oven and dried at 110°C for 6 minutes to remove all solvent. Each prepared laminate was cut into test strips using a 1" specimen tape cutter. Laminate thickness was measured using a Digit-Mike® plus micrometer. Measurements were taken in at least three places on the new laminate where PSA was present to ensure the desired PSA thickness was obtained throughout the sample.

180 Degree Peel Adhesion Test Procedure

Peel adhesion (180°) was tested according to ASTM D3330 and PSTC-1 standards. All tests were conducted on an Instron tester at a peel rate of 12 inches per minute with 2.0-mil PET as the test substrate. A 1-inch wide sample strip of PSA was adhered to a clean stainless steel panel using a 2-kg roller with two passes. Samples were allowed 20 minutes to equilibrate at room temperature before performing the tests. The average of three measurements was reported.

Texture Analyzer Test Procedure

Testing with the TA-XT2i® Texture Analyzer (TA) was performed with a 7mm, stainless steel punch probe with a 1-inch radius of curvature. Using 10-mil PET as the testing substrate, samples were placed under an indexable brass plate to position them for analysis. The following program settings were used:

Pre-test speed: 0.5 mm/sec Test speed: 0.2 mm/sec

Post-test speed: 0.2 mm/sec Test force: 100 grams

Dwell time: 0.5 seconds Trigger force: 1.0 gram

Trigger mode: Auto Collection rate: 200 points/second

A pre-defined macro was run after the completion of each sample to calculate the Peak Force, Area 1:2, Area 2:3, Area 1:3 and the Area Ratio. The average of five measurements was reported.

Static Shear Test Procedure

Static shear testing was completed according to ASTM D3654 and PSTC-7 standards. Samples were prepared for testing by placing a 1-inch wide strip of PSA onto a clean stainless steel test panel. The samples were trimmed to provide a 1 x 1 square inch area of contact and secured with two passes of a 2-kg roller. Metal hangers were secured from the bottom of each test strip and reinforced to ensure failure of the sample occurred at the testing interface. Each test sample was placed in the shear testing apparatus and a 4-pound weight was hung from the metal hanger. Once the test weight is placed on the sample, the timer is reset to zero and time to failure is recorded when the sample detaches from the stainless steel test panel. The average of three measurements was reported.

Measurement of Molecular Weight

The number and weight average molecular weights (M_n and M_w) for each sample were determined by Gel Permeation Chromatography (GPC). The samples were prepared in tetrahydrofuran and analyzed against polystyrene standards using refractive index detection.

Measurement of Glass Transition Temperature (T_g)

The glass transition temperature (T_g) of a particular Example was determined by Differential Scanning Calorimetry (DSC). Approximately 5 to 10 grams of dried material (solventless) in an aluminum pan was placed in the cell of a Differential Scanning Calorimeter. The sample was cooled to $<-150^\circ\text{C}$, then heated to 150°C at a rate of $10^\circ\text{C}/\text{min}$. The T_g was reported as the half-height of the material transition.

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