RAFT POLYMERIZATION OF POLY(BUTYL ACRYLATE) HOMOPOLYMERS AND BLOCK COPIOLYMERS: KINETICS AND PRESSURE-SENSITIVE ADHESIVE CHARACTERIZATION

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A Thesis Submitted to the
University of North Carolina Wilmington in Partial Fulfillment
of the Requirements for the Degree of
Master of Science

Department of Chemistry and Biochemistry

University of North Carolina Wilmington

2011

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ABSTRACT

The RAFT polymerization of butyl acrylate (BA) has been investigated in the presence of cyanomethyl dodecyl trithiocarbonate (CMDTTC) and dibenzyl trithiocarbonate (DBTTC), each a chain transfer agent (CTA). The influence of several experimental parameters, such as trithiocarbonate to initiator molar ratio ([CTA] / [Vazo 67]), butyl acrylate to trithiocarbonate molar ratio ([BA] / [CTA]), and temperature has been studied with respect to polymerization duration, % conversion, correlation between theoretical and experimental molecular weight, and polydispersity index. The kinetics have been followed over the entire conversion range by gas chromatography with flame ionization detection and molecular weight has been determined by size exclusion chromatography with refractive index detection.

Similar trends were observed for both CTAs. Kinetics appear strongly influenced by temperature, and to a lesser extent BA concentration. An increase in the molar ratio of [CTA] / [Vazo 67] resulted in a decrease in molecular weight (MW). Comparison of the data also suggests the existence of an optimal [CTA] / [Vazo 67] ratio; greater than or equal to 3.0 and 4.9 for CMDTTC and DBTTC, respectively. Excellent MW control and low polydispersity index (PDI) were observed throughout the entire polymerization. Surprisingly, MW and PDI were not influenced by temperature. In addition, an increase in [BA] / [CTA] generated a linear increase in MW. Independent of the reaction temperature, MW increased linearly and PDI decreased with monomer conversion.

Additionally, the pressure-sensitive adhesive (PSA) performance and viscoelastic properties of random copolymers were compared to block copolymers of the same acrylic composition. Random and block copolymers were synthesized by free radical and reversible addition-fragmentation chain transfer (RAFT) polymerization, respectively. Triblock
copolymers of BA/acrylic acid (AA) were polymerized in which the AA was positioned into the end-blocks or mid-block, respectively. When compared to random copolymers, both triblock copolymers exhibited higher peel adhesion and tack. However, only the triblock copolymer in which the AA was positioned into the end-blocks gave comparable shear strength. A triblock copolymer of BA/methyl acrylate (MA) was also polymerized in which the MA was strategically positioned into the end-blocks. When compared to random copolymers, the triblock copolymer exhibited similar peel strength and tack. In addition, the triblock copolymer had higher shear strength. This is due to the ability of this structure to form physical networks. The triblock copolymer also possesses no melt flow up to 200 °C.
ACKNOWLEDGEMENTS

I would like to thank the following people who were instrumental in the completion of this thesis:

- Dr. Don Herr (R&D Department, Adhesives Research, Inc.)
- Dr. John Tyrell (Department of Chemistry and Biochemistry, UNCW)
- Dr. Jeremy Morgan (Department of Chemistry and Biochemistry, UNCW)
- Analytical department (Adhesives Research, Inc.) for processing results so quickly
- Adhesives Research, Inc. for the support both financially and professionally
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INTRODUCTION

1.1 Acrylic Pressure Sensitive Adhesives

PSAs are adhesives which bond two surfaces when pressure is applied. The performance of a PSA is typically evaluated by tack, peel strength, and shear strength. Tack is the ability of a PSA to adhere quickly under light pressure. Peel strength refers to the bond strength between a PSA and a substrate after pressure is applied. Shear strength is a measure of the internal strength (i.e. cohesive strength) of a PSA. In general, it is not possible to increase tack and peel strength simultaneously with shear strength. In order to increase shear strength, the cohesive strength of the PSA must be enhanced; however, this will lower the PSAs capability to deform and flow, and accordingly its capability to wet the surface.

A significant portion of a materials ability to perform as a PSA depends on its ability to “wet” a surface. Wetting of a surface does not only depend on interfacial characteristics, but also depends on the ability of the material to flow on the surface with or without applied force. Thus, the characteristics of the adhesive as a “liquid” are important in the generation of adhesive bonds. On the other hand, when the adhesive is peeled back from a surface it should resist the force. That is, it should act as a “solid”. This contradictory behavior is due to the viscoelastic nature of the material. Therefore, a balance of viscous and elastic properties is required to achieve optimum adhesive performance.¹

The viscoelastic properties of an acrylic PSA can be changed by incorporating different monomers during polymerization. Common monomers with a low thermal glass transition temperature \(T_g\) include 2-ethylhexyl acrylate \(T_g\) \(T_{g\,2-EHA} = -60 \, ^\circ C\), isoctyl acrylate \(T_g\) \(T_{g\,IOA} = -50 \, ^\circ C\), and butyl acrylate \(T_g\) \(T_{g\,BA} = -54 \, ^\circ C\).² These “soft” base monomers are typically the
most abundant by weight in an acrylic PSA formulation and impart good deformability and flow ability to the PSA. Structures of “soft” base monomers are shown in Figure 1.

![Structures of “soft” base monomers.](image)

Figure 1: Structures of “soft” base monomers.

Modifying medium T_g monomers include ethyl acrylate (T_g, p(EA) = -24 °C) and methyl acrylate (T_g, p(MA) = 10 °C).^2 These “hard” monomers are responsible for increasing the cohesive strength of the acrylic PSA. Structures of common “hard” monomers are shown in Figure 2.

![Structures of “hard” monomers.](image)

Figure 2: Structures of “hard” monomers.
Carboxylic acid or hydroxyl functionality can also be incorporated into the adhesive backbone during polymerization by utilizing acrylic acid ($T_{g\, p(AA)} = 105 ^\circ C$) or 2-hydroxyethyl acrylate ($T_{g\, p(2\text{-HEA})} = 15 ^\circ C$) monomers, respectively. Acrylic acid is a high $T_g$ monomer that, in addition to increasing cohesive strength, provides a polar moiety for bonding to polar substrates. 2-hydroxyethyl acrylate is also a polar monomer, but has a moderate $T_g$. Both acrylic acid and 2-hydroxyethyl acrylate also provide additional sites for cross-linking which further increases cohesive strength of the acrylic PSA. Structures of functional monomers are shown in Figure 3.

![Acrylic Acid and 2-Hydroxyethyl Acrylate](image)

Figure 3: Structures of functional monomers.

The viscoelastic properties of a PSA can also be controlled by changes in polymer microstructure (*i.e.*, cross-link density). In general, increasing cross-link density tends to increase a PSA's cohesive strength while decreasing their deformability. Consequently, with the increase in cross-link density, shear strength increases, while tack and peel strength decreases.

Materials viscoelastic properties can be determined via dynamic mechanical analysis (DMA). DMA can be simply described as applying an oscillatory deformation (*i.e.*, strain) to a sample and analyzing the materials response to that force. From this, one calculates properties like the tendency to flow ($G''$) and the stiffness ($G'$). These properties are often described as the ability to lose energy as heat (damping) and the ability to recover from deformation (elasticity).
The degree to which the adhesive exhibits more liquid-like or solid-like properties is dependent upon temperature as well as time or frequency. In adhesive applications initial bond formation occurs at low deformation rates whereas the debonding step requires high strain rates. With the help of DMA, viscoelastic properties measured at low frequencies correspond to bond formation while high frequencies characterize debonding behavior. The latter describes a materials shear strength and the former relates to a PSAs tack and peel strength. Therefore, polymer chemists use DMA testing to predict or evaluate how manipulation of a PSAs viscoelastic behavior influences adhesive performance.\(^5\)

1.2 Free radical polymerization

Currently the most widely used process for acrylic PSA synthesis is free radical polymerization. The main factors responsible for its popularity are:

- It can be used with a large variety of monomers;
- It is tolerant to a wide range of functional groups and reaction conditions;
- It is simple to implement and inexpensive in relation to competitive technologies.

Free radical polymerization is a technique that can be broken down into 3 steps (Figure 4):

1. *Initiation.* Chain initiation involves formation of two free radicals (2 \(R^\cdot\)) by the homolytic dissociation of the initiator. Initiating radicals may be generated via thermal, redox, or photochemical reactions. This is followed by the addition of a radical (\(R^\cdot\)) to a monomer molecule (M), to yield the initial propagating species (\(P_1^\cdot\)). Because the formation of the radicals is generally slower than their addition to the monomer, the first step determines the rate of initiation.
2. *Propagation*. The propagation step is the successive addition of a large number of monomer molecules (M) to the primary active radical center (P<sub>n</sub>·). Each addition yields a new active radical (P<sub>n+1</sub>·) which is larger than P<sub>n</sub>· by one monomer molecule. In order to grow long polymer chains by free radical polymerization, the rate of propagation must be significantly faster (~ 1000 times) than the rates of initiation or termination.\(^6\)

3. *Termination*. Chain termination irreversibly terminates the growth of the polymer, leading to so-called “dead” polymer. The two most common mechanisms are combination (a) or disproportionation (b). Other possible mechanisms for termination are coupling of a growing chain with a primary radical from the initiator (c), reaction of a growing chain with a compound stabilizing radicals such as oxygen (d), or transfer of a radical to another molecule (e.g., solvent, impurities) present in the system (e).
Even though free radical polymerization is widely used, some notable limitations are present. Due to an extremely high termination rate (not rate constant) initiator must be continuously added throughout the polymerization. Quantitative effects of repeated initiator addition are difficult to determine, making chain growth almost uncontrollable. As a result, polymers created by free radical polymerization exhibit relatively broad polydispersity indexes (PDI = $M_w / M_n > 2$, where $M_w$ is the weight average molecular weight and $M_n$ is the number average molecular weight). Also, the polymerization of elaborate macromolecular architectures, such as block copolymers, is not possible with free radical polymerization.
1.3 Living radical polymerization

Although for many applications no strict control over the MW, the PDI, or the chemical composition of the polymer is required, there is a large interest in architectures such as block copolymers, which cannot be made via conventional free radical polymerization. Traditionally, block copolymers have always been made via living anionic polymerization. The concept of living anionic polymerization was first demonstrated in 1956 by Szwarc\textsuperscript{7,8} who stated that for a polymerization to be considered “living” it should meet the following criteria:

- The number of polymer chains is constant during polymerization;
- The polymerization proceeds to full conversion. Further addition of monomer leads to continued polymerization;
- The number average molecular weight ($M_n$) can be controlled by the reaction stoichiometry;
- The $M_n$ is linearly dependent on conversion;
- A narrow PDI is achieved.

During the last few decades, several new techniques were discovered which allowed the advancement of living polymerization using free radical chemistry. These techniques are referred to as living radical polymerizations. To confer living character on a free radical polymerization, it is necessary to eliminate all processes that terminate chains irreversibly. Thus, living radical polymerization only becomes possible in the presence of reagents that react with the propagating radicals ($P_n\cdot$) by reversible deactivation (Figure 5) or reversible chain transfer (Figure 6) so that the majority of chains are maintained in a dormant form ($P_n\cdot X$).\textsuperscript{9} Rapid equilibrium between the active and dormant forms ensures that all chains possess an equal
chance for growth. Under these conditions, the molecular weight increases linearly with conversion and the PDI can be very narrow.

![Diagram](image1)

Figure 5: Reversible deactivation mechanism.\(^9\)

![Diagram](image2)

Figure 6: Reversible chain transfer mechanism.\(^9\)

Two examples of reversible deactivation are nitroxide-mediated polymerization (NMP)\(^{10}\) and atom transfer radical polymerization (ATRP)\(^{11,12}\). Reversible addition-fragmentation chain transfer (RAFT)\(^{13,14}\) polymerization is an example of reversible chain transfer. In reversible deactivation, the polymer chain is end-capped with a moiety that can reversibly undergo homolytical cleavage. In NMP, this moiety is a nitroxide, while in ATRP, a halide is reversibly transferred to a transition-metal complex. In processes based on reversible chain transfer, there is a fast exchange of growing radicals via a transfer agent. In the RAFT process, thiocarbonylthio compounds are responsible for this exchange, which proceeds via an intermediate radical.

Of the three available techniques to mediate a living free radical polymerization, the RAFT process has proven to be the most versatile. It is compatible with a broad range of monomers\(^{15}\) and can be carried out under “normal” free radical polymerization conditions.\(^{16}\)
Both NMP and ATRP are only applicable to a limited range of monomers, require reagents that are expensive and/or difficult to remove, and require special polymerization conditions (e.g. high reaction temperatures). Due to its versatility, RAFT polymerization is the focus of this thesis and will now be discussed in more detail.

1.4 Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization

RAFT polymerization was developed by Rizzardo and coworkers at the Commonwealth Scientific and Industrial Research Organization (CSIRO) in 1998. RAFT has been found to polymerize a wide range of monomers, including styrenic, acrylamides, acrylates, and vinyl acetate. RAFT polymerizations are also carried out in the same conditions as free radical polymerization, except for the addition of a chain transfer agent (CTA), which is also referred to as the RAFT agent. All RAFT agents are thiocarbonylthio compounds, and include, for example, dithioesters, dithiocarbamates, trithiocarbonates, and xanthates (Figure 7). The effectiveness of the RAFT agent depends on the monomer being polymerized and the properties of the Z and R groups, respectively. The Z group should activate the C=S double bond towards radical addition, whereas the R group should be a good free radical leaving group, as well as a good reinitiating group.

\[ \begin{align*}
\text{Z} & \quad \text{S} & \quad \text{R} \\
\text{Z} & \quad \text{N} & \quad \text{S} & \quad \text{R} \\
\text{Z} & \quad \text{S} & \quad \text{S} & \quad \text{R} \\
\text{Z} & \quad \text{O} & \quad \text{S} & \quad \text{R}
\end{align*} \]

Dithioester  Dithiocarbamate  Trithiocarbonate  Xanthate

Figure 7: Structures of different classes of reagents currently used as RAFT agents.
RAFT polymerization is a technique that can be broken down into 5 steps (Figure 8):

1. **Initiation.** In the early stages of the polymerization, an initiator generates radicals that combine with monomer units to form polymer chains. Since new chains are constantly created by means of initiator decomposition, the total amount of initiator should be low in comparison with the amount of RAFT agent (1).

2. **Pre-Equilibrium.** A propagating chain ($P_n^-$) becomes capped when the radical attacks the carbon-sulfur double bond of the RAFT agent (1). The resulting radical intermediate (2) fragments into a dormant polymeric thiocarbonylthio compound (3) and a reinitiating radical ($R^\cdot$). The transformation of RAFT agent (1) into the dormant polymeric thiocarbonylthio compound (3) should be rapid to ensure that all polymer chains start growing at the same time. That is why the leaving group of the original RAFT agent (*i.e.*, the R group) needs to be chosen in such a way that it is a better homolytic leaving group than the polymer chain ($P_n$). Furthermore, the expelled radical ($R^\cdot$) should be a good reinitiating group.

3. **Chain Propagation and Reinitiation.** Reaction of the new radical ($R^\cdot$) with monomer forms a new propagating radical ($P_m^-$).

4. **Main Equilibrium.** The new propagating radical ($P_m^-$) reacts with the dormant polymeric thiocarbonylthio compound (3), forming a new dormant polymeric thiocarbonylthio compound (5) and another propagating radical ($P_n^-$). Rapid equilibrium between the propagating radicals ($P_n^-$ and $P_m^-$) and the dormant polymeric thiocarbonylthio compound provides equal probability for all chains to grow at the same rate, leading to a linear evolution of the molecular weight with conversion and
very narrow polydispersity. The efficiency of this step determines the living character of the polymerization.

5. **Termination.** Throughout the polymerization some “dead” polymer chains will be formed. Chain termination may occur via coupling reactions of two active centers (referred to as combination), or atomic transfer between active chains (termed disproportionation). However, this step should be minimized in order to achieve living behavior.

Figure 8: General RAFT polymerization mechanism.
Due to the lack of termination reactions during a RAFT polymerization, the theoretical number average molecular weight, $M_{n(\text{theoretical})}$, can be calculated using the following equation:\(^{26}\)

\[
M_{n(\text{theoretical})} = \frac{[M]_0}{[\text{RAFT}]} \times \text{conversion} \times M_i \quad (\text{Equation 1})
\]

where $[\text{RAFT}]_0$ is the initial RAFT concentration, $[M]_0$ is the initial monomer concentration, and $M_i$ is the monomer molecular weight. This equation assumes that the efficiency of the RAFT agent is 100% (i.e., all RAFT agents are attached to a polymer chain), termination events (chain transfer to monomer and radical-radical termination) are negligible, and the small number of chains formed from the initiator are not accounted for. Thus, based on equation 1, a molecular weight range of well-defined polymers can be polymerized with different molecular weights by simply varying the ratio of monomer to RAFT agent.

1.5 Block copolymers by RAFT

Block copolymers are linear copolymers which consist of long sequences or blocks of constant composition linked by covalent bonds. As seen in Figure 9, the simplest arrangement is the diblock structure, commonly referred to as an A-B block copolymer, which is composed of one segment of “A” repeat units and one segment of “B” repeat units. Another type is the triblock, or A-B-A, block copolymer structure, consisting of a single segment of B repeat units located between two segments of A repeat units.
As mentioned before, it is generally impossible to produce block copolymers by conventional free radical polymerization. Therefore, living radical polymerization is used to polymerize block copolymers of desired chemical composition and molar mass, with a narrow PDI. As already mentioned, there are three main living radical polymerization techniques which have been used during the last decades (i.e. NMP, ATRP, and RAFT), and usually all of them can be used for the polymerization of block copolymers. However, due to its versatility, RAFT will be used for the polymerization of all block copolymers described in this thesis.

Following consumption of the monomer in a RAFT polymerization, the propagating center remains active, sometimes for days. The subsequent initiation of a different monomer by the first block leads to diblock copolymers. Monomer addition can be repeated to form triblock and multiblock polymers. One of the most interesting effects of a block copolymer occurs when the two blocks, A and B, are mutually incompatible. In this case, a phase separation occurs. However, due to the covalent bond between blocks A and B, phase separation cannot proceed to a macroscopic scale. Instead, micro-domains rich in each of the two blocks are formed. This
behavior is known to influence the physical properties of a block copolymer. The properties that are dramatically affected are: elastomeric behavior, melt rheology, and toughness.\textsuperscript{27}

The choice of RAFT agent is of particular importance to the synthesis of block copolymers.\textsuperscript{28} Trithiocarbonates are known to provide excellent control and little or no retardation in RAFT polymerizations of acrylates.\textsuperscript{29} The outstanding feature of trithiocarbonates is that they can be prepared with either one or two good homolytic leaving groups. A trithiocarbonate with one good homolytic leaving group allows for the polymerization of A-B diblock copolymers in two sequential monomer addition steps (Figure 10). In the first polymerization step, monomer is inserted between the -(C=S)S- moiety and the free radical leaving group (R). After the first step is complete, the second monomer is inserted between the -(C=S)S- moiety and the end of the first block, with the RAFT functionality remaining at the chain end. Higher order (ABA, ABC, etc.) blocks are also possible by sequential addition of monomer(s).

![Figure 10: General polymerization of A-B diblock copolymer.](image)

A trithiocarbonate with two good homolytic leaving groups allows for the polymerization of A-B-A triblock copolymers in two sequential monomer addition steps instead of three (Figure 11). The symmetry of this compound ensures that both arms are approximately the same length and composition. In the first polymerization step, monomer is inserted between both leaving...
groups (R) and the \(-\text{S(C=S)}-\) moiety, and the \(-\text{S(C=S)}-\) moiety remains in the middle of the polymer chain. When chain extending the first block, the second block is built in the middle of the polymer chain, and the first block will shift to the outside of the polymer chain.

\[
\begin{align*}
\text{R} & \quad \text{S} \quad \text{S} \quad \text{R} \\
& \quad \text{M}_A \quad \text{Initiator} \\
& \quad \text{RA}_n \text{S} \quad \text{S} \quad \text{A}_n \text{R} \\
& \quad \text{M}_B \quad \text{Initiator} \\
& \quad \text{RA}_n \text{B}_m \text{S} \quad \text{S} \quad \text{B}_m \text{A}_n \text{R}
\end{align*}
\]

Figure 11: General polymerization of A-B-A triblock copolymer.

The order of constructing the blocks of a block copolymer is very important during a RAFT polymerization.\(^2^8\) One requirement is that the leaving group ability of propagating radical \(\text{A} \cdot\) is comparable to or greater than that of propagating radical \(\text{B} \cdot\). If propagating radical \(\text{B} \cdot\) is a better leaving group, the adduct radical will partition strongly in favor of the starting material (Figure 12). Thus, no block copolymer polymerization will take place. For example, during the polymerization of poly(methyl methacrylate)-block-poly(styrene), the methyl methacrylate block should be prepared first.\(^2^8\) The second step would include the addition of styrene to the methyl methacrylate block. Ultimately, adding the blocks in the correct order leads to a well-defined block copolymer with narrow PDI.

\[
\begin{align*}
\text{B} \cdot & \quad \text{S} \quad \text{S} \quad \text{A} \\
& \quad \text{Z} & \quad \text{Z} & \quad \text{Z} \\
& \quad \text{B} \cdot & \quad \text{S} \quad \text{S} \quad \text{A} \\
& \quad \text{Z} & \quad \text{Z} & \quad \text{Z} \\
& \quad \text{B} \cdot & \quad \text{S} \quad \text{S} \quad \text{A} \\
& \quad \text{Z} & \quad \text{Z} & \quad \text{Z}
\end{align*}
\]

Figure 12: General equilibrium for proper block construction.\(^2^8\)
The molar mass of the entire block copolymer is predicted by using a slightly modified version of equation 1. In the case of RAFT-mediated block copolymerization, \( M_n^{(theoretical)} \) is calculated using the following equation:26

\[
M_n^{(theoretical)} = M_{n,macro-RAFT} + \frac{[M_0]}{[RAFT]_0} \times \text{conversion} \times M_i \quad (Equation \ 2)
\]

where \( M_{n,macro-RAFT} \) represents the experimentally observed \( M_n \) of the starting block. The other parameters are the same as for equation 1.

1.6 Objective

The first objective of this thesis is to study in detail the RAFT polymerization of BA in the presence of CMDTTC or DBTTC. The influence of several experimental parameters on the kinetics and control of MW, such as trithiocarbonate to initiator molar ratio ([CTA] / [Vazo 67]), BA to trithiocarbonate molar ratio ([BA] / [CTA]), and temperature will be investigated. Knowledge of each experimental parameter will help facilitate the synthesis of block copolymers with desirable characteristics.

The second objective of this thesis is to compare the PSA performance and viscoelastic properties of random copolymers to block copolymers of the same acrylic composition. Random copolymers will be synthesized by free radical polymerization while block copolymers will be synthesized by RAFT polymerization. The base monomer composition will be comprised of butyl acrylate or a combination of butyl acrylate/methyl acrylate. When applicable, carboxylic acid functionality will be incorporated into the polymer backbone during polymerization by utilizing acrylic acid. The resulting PSAs will be fully characterized by various physical and
analytical test methods. This will give insight into how controlled monomer placement compares to conventional random polymerization in terms of PSA performance.
EXPERIMENTAL

2.1 Materials

Butyl acrylate (BASF, ≥ 99.5%), methyl acrylate (Dow Chemical, ≥ 99.5%), glacial acrylic acid (Arkema, > 99.0%), ethyl acetate (Brenntag Northeast, Inc., > 99.5%), isopropyl alcohol (IPA, Shell Chemical, 99%), tetrahydrofuran (BASF, ≥ 99.9%), methyl ethyl ketone (MEK, Brenntag, ≥ 99.5), Vazo 67 (E.I. Dupont Company, Inc., > 98%), dibenzyltrithiocarbonate (Strem Chemical, > 97%), cyanomethyl dodecyl thio dicarbonate (Aldrich, 98%), and trimethylolpropane tris(2-methyl-1-aziridine propionate) (Polyaziridine, LLC) were all used as received.

The structures of CMDTTC and DBTTC RAFT agents are shown in Figure 13.

![Figure 13: Structures of CMDTTC and DBTTC RAFT agents.](image)
2.2 Characterization of polymer samples

All analytical and physical test methods, which were used for polymer characterization, are documented below.

2.2.1 Solution Viscosity

Solution viscosities were measured using a Brookfield RVT viscometer. Spindle and spindle speeds were selected such that a torque value of 20-80% was achieved for optimal accuracy.

2.2.2 Differential Scanning Calorimetry

Solution polymer was directly cast onto silicone primed polyester. All samples were dried for 5 min at 120 °C. 10-15mg of dried polymer was placed into a TA Instruments Tzero aluminum low-mass pan. A TA Instruments Tzero aluminum lid was placed onto the pan. The pan and lid were then hermetically sealed. Samples were analyzed on a TA Instruments Q2000 Differential Scanning Calorimeter (DSC) from -100 to 200 °C at a heating rate of 20 °C/min. All polymers were analyzed twice. The first pass was used to erase its thermal history and the second pass was used for data collection. Universal Analysis 2000 software was used to interpret the thermograms.

2.2.3 Dynamic Mechanical Analysis

Dried polymer was layered until a thickness of 15mil was achieved. Samples were analyzed using a TA Instruments AR 2000 controlled stress rheometer, in the oscillatory mode, with 25mm parallel plate geometry and environmental temperature controlled oven.
The 25 ºC frequency sweep was analyzed from 0.01 to 628 rad/sec, using 1% strain. The temperature step was analyzed from -50 to 200 ºC, testing at a frequency of 1 rad/sec and 1% strain every 3 ºC with a 1 min soak time at each temperature prior to collecting data.

2.2.4 Molecular Weight Analysis

Size exclusion chromatography (SEC) was performed on a Polymer Laboratories PL-GPC 50 Plus system comprising an auto injector, a Polymer Laboratories 10µm particle size guard column (50mm x 7.5mm ID), a Polymer Laboratories 10µm particle size mixed-B column (300mm x 7.5mm ID), and a refractive index detector. A constant column temperature of 35 ºC was maintained throughout. Polymethyl methacrylate (PMMA) standards ranging from 690 to 1,944,000 g/mol were used for calibration. All samples were dried for 5 min at 120 ºC (Note: No cross-linker was added to PSAs A, B, C, or D). Dried polymer was weighed out to 30mg and 10mL of sulfur-spiked tetrahydrofuran (THF) was added. The sample sat overnight at room temperature to ensure adequate dissolution. Prior to injection, the sample and standards were filtered through VWR 0.45µm filters. The eluent was stabilized THF with a flow rate of 1mL/min. The injection volume was 100µL. Number average molecular weight (M_n(SEC)), weight average molecular weight (M_w(SEC)), and molecular weight distribution (i.e., polydispersity index, PDI = M_w/M_n) from SEC chromatograms were calculated relative to PMMA standards.

2.2.5 Residual Monomer Analysis

Residual monomer analysis was performed by liquid-injection using a PerkinElmer Clarus 600 Gas Chromatograph (GC) comprising an auto injector, a Varian CP-SIL 19CB (14% cyanopropyl-phenyl, 86% dimethylpolysiloxane) column (60m x 0.32mm ID), and a flame
ionization detector (FID). The standard stock solution was prepared by adding 1mL of monomer to a 20mL volumetric flask and diluting to volume with THF. Working standards were prepared by adding 0.25mL, 0.50mL, and 1.0mL of the standard stock solution to a 100mL volumetric flask and diluting to volume with THF. Approximately 1g of solution polymer was weighed into a 30mL vial. 10mL of THF was added and all samples were shaken vigorously to ensure complete dissolution. All samples and standards were prepared in singlet. The injection temperature was 230 ºC and the injection volume was 1µL, with a 50:1 split ratio. The GC oven was ramped from 40 ºC to 220 ºC at 10 ºC/min and was then held at 220 ºC for 12 minutes. The carrier gas was helium at a constant pressure of 14psi. The FID was 250 ºC. First-order calibration curves were created from the working standards. Percent residual monomer was calculated from the calibration curve. The following equation was then used to calculate % conversion:

\[
\% \text{ Conversion} = \left(\frac{\% \text{ Theoretical Solids} - \% \text{ Residual Monomer}}{\% \text{ Theoretical Solids}}\right) \times 100 \quad (Equation \ 3)
\]

2.2.6 180º Peel Adhesion

All samples were directly cast onto 2.0mil polyester at approximately 1.5mil adhesive thickness. The appropriate drying conditions for each polymer are located in its respective section. Samples (1” x 5”) were applied to a stainless steel (SS) or high density polyethylene (HDPE) panel while mechanically rolling the sample lengthwise in both directions with a 4.5 pound roller. The samples were allowed to dwell for 15 min or 24 h at 23 ºC and 50% relative humidity. The panel was then clamped into the bottom jaw of the MTS Alliance RT/1, the sample doubled back at an angle of 180º and clamped into the upper jaw. All samples (n=3)
were then pulled a minimum of 4 inches at a crosshead speed of 12 inches/min. The peel force
data was measured between 1 and 4 inches then averaged and recorded as peel adhesion.

2.2.7 Shear Strength

All shear tests were carried out on stainless steel panels with strips (0.5” x 3”) of the
dried adhesive coated film. One end of each adhesive strip was joined to the stainless steel panel
by mechanically rolling the sample with a 4.5 pound roller. A contact area of 0.5” x 0.5” was
used for all samples. The other end was then connected to a 500g weight. All samples were then
allowed to dwell for 15 min at 23 ºC and 50% relative humidity prior to testing. A
Chem Instruments 30 Bank Shear Tester with digital clock was then used to measure shear time
to failure. All samples were tested in triplicate.

2.2.8 Probe Tack

A 1” x 1” square was cut from the dried adhesive coated film. The adhesive was then
applied, face-down, to a brass annular ring. The brass annular ring was then placed directly into
the probe well. The probe test speed was set to 1cm. A dwell time of either 1 or 10 sec was
used. All samples (n=3) were tested at 23 ºC and 50% relative humidity using a Polyken Probe
Tack Tester.

2.2.9 Precision Oven Solids

The weight of an empty aluminum pan was initially determined. The cap was then
removed from a disposable 1-cc syringe and filled to the 0.6-cc mark with liquid polymer. The
syringe tip was cleaned with lint free tissue and the cap was immediately replaced. The filled
syringe, with cap, was then placed on top of the empty aluminum pan and its weight was measured. The empty aluminum pan was then moved to a clean surface and the liquid polymer was evenly dispensed around the bottom of the pan. The cap was then placed back onto the syringe and its weight was measured. All samples were dried for 60 min at 150 °C. After 60 min the aluminum pan and residue were measured. The following equations were used to determine % solids of solution polymer:

\[
\text{Wet Weight(g)} = [(\text{Pan} + \text{Filled Syringe}) - \text{Pan}] - \text{Emptied Syringe} \quad (\text{Equation 4})
\]

\[
\text{Dry Weight(g)} = (\text{Pan} + \text{Residue}) - \text{Pan} \quad (\text{Equation 5})
\]

\[
\% \text{Solids}_{\text{measured}} = \left(\frac{\text{Dry Weight}}{\text{Wet Weight}}\right) \times 100 \quad (\text{Equation 6})
\]

2.3 Polymerization of polymer samples

An outline of the polymerization procedures are documented below.

2.3.1 Polymerization of butyl acrylate using CMDTTC as RAFT agent

A typical butyl acrylate homopolymer synthesis was carried out as follows: 150g of ethyl acetate was added into a 1L vessel equipped with a heating jacket, stirrer, feed tanks, and nitrogen gas inlet. The vessel was sealed under nitrogen atmosphere following three nitrogen-vacuum cycles to remove dissolved oxygen. The vessel was heated to 75 °C over a period of 30 min. A reagent mixture feed of 200g butyl acrylate (1.56mol), 1.5g CMDTTC (4.7mmol), 0.2g Vazo 67 (1.04mmol), and 50g ethyl acetate was added over a period of 2 h. Over the 2 h reagent feed the contents were mixed at 100 rpm while maintaining a reaction temperature of 74-76 °C. The reaction conditions were maintained for an additional 3 h following completion of the reagent feed at which point > 90% of the monomer was consumed to generate a homopolymer of
theoretical $M_n$ of 40,566 g/mol. The resulting solution polymer was then cooled to ambient temperature and discharged from the vessel.

**Additional Studies**

The effects of CMDTTC on BA polymerization were determined by varying the molar ratio of CMDTTC to Vazo 67 from 1.5 to 13.5 while keeping the molar ratio of BA to Vazo 67 constant. The experimental conditions are outlined in Table 1. For polymerization kinetics data, samples were withdrawn at predetermined time points. Number average molecular weight ($M_n$(sec)), weight average molecular weight ($M_w$(sec)), molecular weight distribution (PDI), and % conversion as a function of time were determined.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature (°C)</th>
<th>[BA] (mol L$^{-1}$)</th>
<th>[CMDTTC] (mmol L$^{-1}$)</th>
<th>[Vazo 67] (mmol L$^{-1}$)</th>
<th>[CMDTTC]/[Vazo 67]</th>
<th>[BA]/[Vazo 67]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75</td>
<td>7</td>
<td>7</td>
<td>4.7</td>
<td>1.5</td>
<td>1489</td>
</tr>
<tr>
<td>2</td>
<td>75</td>
<td>7</td>
<td>14.1</td>
<td>4.7</td>
<td>3</td>
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<td>75</td>
<td>7</td>
<td>33.3</td>
<td>4.7</td>
<td>7.1</td>
<td>1489</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
<td>7</td>
<td>63.6</td>
<td>4.7</td>
<td>13.5</td>
<td>1489</td>
</tr>
</tbody>
</table>

Table 1: Experimental conditions for BA polymerization in the presence of various [CMDTTC] / [Vazo 67] ratios.

The effects of varying the molar ratio of BA to CMDTTC from 330.2 to 660.4 while keeping the molar ratio of CMDTTC to Vazo 67 constant were determined. The experimental conditions are outlined in Table 2. Number average molecular weight ($M_n$(sec)), weight average molecular weight ($M_w$(sec)), molecular weight distribution (PDI), and % conversion were determined.
The effects of temperature on BA polymerization, when using CMDTTC as RAFT agent, were determined by varying the polymerization temperature from 65 to 85 °C. The experimental conditions are outlined in Table 3. For polymerization kinetics data, samples were withdrawn at predetermined time points. Number average molecular weight (\(M_n(\text{sec})\)), weight average molecular weight (\(M_w(\text{sec})\)), molecular weight distribution (PDI), and % conversion as a function of time were determined.

### Table 2: Experimental conditions for BA polymerization in the presence of various [BA] / [CMDTTC] ratios.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature (°C)</th>
<th>[BA] (mol L(^{-1}))</th>
<th>[CMDTTC] (mmol L(^{-1}))</th>
<th>[Vazo 67] (mmol L(^{-1}))</th>
<th>[CMDTTC]/[Vazo 67]</th>
<th>[BA]/[CMDTTC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>75</td>
<td>7</td>
<td>21.2</td>
<td>4.7</td>
<td>4.5</td>
<td>330.2</td>
</tr>
<tr>
<td>6</td>
<td>75</td>
<td>8.7</td>
<td>21.2</td>
<td>4.7</td>
<td>4.5</td>
<td>410.4</td>
</tr>
<tr>
<td>7</td>
<td>75</td>
<td>10.5</td>
<td>21.2</td>
<td>4.7</td>
<td>4.5</td>
<td>495.3</td>
</tr>
<tr>
<td>8</td>
<td>75</td>
<td>14</td>
<td>21.2</td>
<td>4.7</td>
<td>4.5</td>
<td>660.4</td>
</tr>
</tbody>
</table>

Table 3: Experimental conditions to determine effects of temperature on BA polymerization, when using CMDTTC as RAFT agent.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature (°C)</th>
<th>[BA] (mol L(^{-1}))</th>
<th>[CMDTTC] (mmol L(^{-1}))</th>
<th>[Vazo 67] (mmol L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>65</td>
<td>7</td>
<td>21.2</td>
<td>4.7</td>
</tr>
<tr>
<td>10</td>
<td>75</td>
<td>7</td>
<td>21.2</td>
<td>4.7</td>
</tr>
<tr>
<td>11</td>
<td>85</td>
<td>7</td>
<td>21.2</td>
<td>4.7</td>
</tr>
</tbody>
</table>

2.3.2 Polymerization of butyl acrylate using DBTTC as RAFT agent

A typical butyl acrylate homopolymer synthesis was carried out as follows: 150g of ethyl acetate was added into a 1L vessel equipped with a heating jacket, stirrer, feed tanks, and nitrogen gas inlet. The vessel was sealed under nitrogen atmosphere following three nitrogen-vacuum cycles to remove dissolved oxygen. The vessel was heated to 75 °C over a period of 30 min. A reagent mixture feed of 200g butyl acrylate (1.56mol), 1.5g DBTTC (5.16mmol), 0.2g Vazo 67 (1.04mmol), and 50g ethyl acetate was added over a period of 2 h. Over the 2 h reagent
feed the contents were mixed at 100 rpm while maintaining a reaction temperature of 74-76 °C. The reaction conditions were maintained for an additional 3 h following completion of the reagent feed at which point > 90% of the monomer was consumed to generate a homopolymer of theoretical Mₙ of 35,228 g/mol. The resulting solution polymer was then cooled to ambient temperature and discharged from the vessel.

Additional Studies

The effects of DBTTC on BA polymerization were determined by varying the molar ratio of DBTTC to Vazo 67 from 1.1 to 10.7 while keeping the molar ratio of BA to Vazo 67 constant. The experimental conditions are outlined in Table 4. For polymerization kinetics data, samples were withdrawn at predetermined time points. Number average molecular weight (Mₙ(sec)), weight average molecular weight (M_w(sec)), molecular weight distribution (PDI), and % conversion as a function of time were determined.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature (°C)</th>
<th>[BA] (mol L⁻¹)</th>
<th>[DBTTC] (mmol L⁻¹)</th>
<th>[Vazo 67] (mmol L⁻¹)</th>
<th>[DBTTC]/[Vazo 67]</th>
<th>[BA]/[Vazo 67]</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>75</td>
<td>7</td>
<td>5.2</td>
<td>4.7</td>
<td>1.1</td>
<td>1489</td>
</tr>
<tr>
<td>13</td>
<td>75</td>
<td>7</td>
<td>23.2</td>
<td>4.7</td>
<td>4.9</td>
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</tr>
<tr>
<td>14</td>
<td>75</td>
<td>7</td>
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<td>4.7</td>
<td>7.4</td>
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</tr>
<tr>
<td>15</td>
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<td>7</td>
<td>50.5</td>
<td>4.7</td>
<td>10.7</td>
<td>1489</td>
</tr>
</tbody>
</table>

Table 4: Experimental conditions for BA polymerization in the presence of various [DBTTC]/[Vazo 67] ratios.

The effects of varying the molar ratio of BA to DBTTC from 301.7 to 679.6 while keeping the molar ratio of DBTTC to Vazo 67 constant were determined. The experimental conditions are outlined in Table 5. Number average molecular weight (Mₙ(sec)), weight average molecular weight (M_w(sec)), molecular weight distribution (PDI), and % conversion were determined.
Table 5: Experimental conditions for BA polymerization in the presence of various [BA] / [DBTTC] ratios.

The effects of temperature on BA polymerization, when using DBTTC as RAFT agent, were determined by varying the polymerization temperature from 65 to 85 ºC. The experimental conditions are outlined in Table 6. For polymerization kinetics data, samples were withdrawn at predetermined time points. Number average molecular weight \( (M_n(\text{sec})) \), weight average molecular weight \( (M_w(\text{sec})) \), molecular weight distribution \( (\text{PDI}) \), and % conversion as a function of time were determined.

Table 6: Experimental conditions to determine effects of temperature on BA polymerization, when using DBTTC as RAFT agent.

2.3.3  Polymerization of triblock poly(butyl acrylate)-block-poly(butyl acrylate/acrylic acid)-block-poly(butyl acrylate) using DBTTC as RAFT agent

An acrylic copolymer with reactive functionality positioned in the mid-block was prepared as follows: 150g of ethyl acetate was added into a 1L vessel equipped with a heating jacket, stirrer, feed tanks, and nitrogen gas inlet. The vessel was sealed under nitrogen atmosphere following three nitrogen-vacuum cycles to remove dissolved oxygen. The vessel was heated to 75 ºC over a period of 30 min. A reagent mixture feed of 350g butyl acrylate
(2.73mol), 1.5g DBTTC (5.16mmol), and 0.2g Vazo 67 (1.04mmol) was added over a period of 2 h. Over the 2 h reagent feed the contents were mixed at 100 rpm while maintaining a reaction temperature of 74-76 ºC. The reaction conditions were maintained for an additional 3 h following completion of the reagent feed at which point >90% of the monomer was consumed to generate nonreactive end-blocks of theoretical M_n of 31,102 g/mol. A reagent mixture feed of 33.25g butyl acrylate (0.26mol), 1.75g acrylic acid (0.024mol), 0.2g Vazo 67 (1.04mmol), and 15g of ethyl acetate was then added over a period of 20 min. Over the 20 min reagent feed the contents were mixed at 100 rpm while maintaining a reaction temperature of 74-76 ºC. The reaction conditions were maintained for an additional 2 h following completion of the reagent feed at which point > 90% of the monomer was consumed to generate a reactive mid-block of theoretical M_n of 5,809 g/mol. The resulting solution polymer was then cooled to ambient temperature and discharged from the vessel.

Cross-linking of acrylic copolymer

100% based on moles of acrylic acid were targeted for cross-linking using Trimethylolpropane tris(2-methyl-1-aziridne propionate) (PZ-28) cross-linker on equal molar equivalence. PZ-28 was diluted to 10 wt% concentration in ethyl acetate which was added into the acrylic copolymer solution with high speed mixing (~1500 rpm) for 5 min. Unless noted otherwise, the adhesive composition was dried for 5 min at 120 ºC to eliminate the solvent, followed by 24 h at 65 ºC to ensure complete cross-linking.

This polymer will be designated as PSA A from this point forward.
2.3.4 Polymerization of triblock poly(butyl acrylate/acrylic acid)-block-poly(butyl acrylate)-
block-poly(butyl acrylate/acrylic acid) using DBTTC as RAFT agent

An acrylic copolymer with reactive functionality positioned in the end-blocks was prepared as follows: 150g of ethyl acetate was added into a 1L vessel equipped with a heating jacket, stirrer, feed tanks, and nitrogen gas inlet. The vessel was sealed under nitrogen atmosphere following three nitrogen-vacuum cycles to remove dissolved oxygen. The vessel was heated to 75 ºC over a period of 30 min. A reagent mixture feed of 33.25g butyl acrylate (0.26mol), 1.75g acrylic acid (0.024mol), 1.5g DBTTC (5.16mmol), 0.2g Vazo 67 (1.04mmol), and 15g ethyl acetate was added over a period of 20 min. Over the 20 min reagent feed the contents were mixed at 100 rpm while maintaining a reaction temperature of 74-76 ºC. The reaction conditions were maintained for an additional 2 h following completion of the reagent feed at which point > 90% of the monomer was consumed to generate reactive end-blocks of theoretical Mn of 3,165 g/mol. A reagent mixture feed of 350g butyl acrylate (2.73mol) and 0.2g Vazo 67 (1.04mmol) was then added over a period of 2 h. Over the 2 h reagent feed the contents were mixed at 100 rpm while maintaining a reaction temperature of 74-76 ºC. The reaction conditions were maintained for an additional 3 h following completion of the reagent feed at which point > 90% of the monomer was consumed to generate a nonreactive mid-block of theoretical Mn of 56,970 g/mol. The resulting solution polymer was then cooled to ambient temperature and discharged from the vessel.

Cross-linking of acrylic copolymer

100% based on moles of acrylic acid were targeted for cross-linking using PZ-28 cross-linker on equal molar equivalence. PZ-28 was diluted to 10 wt% concentration in ethyl acetate which was added into the acrylic copolymer solution with high speed mixing (~1500 rpm) for 5
min. Unless noted otherwise, the adhesive composition was dried for 5 min at 120 °C to eliminate the solvent, followed by 24 h at 65 °C to ensure complete cross-linking. This polymer will be designated as PSA B from this point forward.

2.3.5 Polymerization of random poly(butyl acrylate/acrylic acid) using DBTTC as RAFT agent.

An acrylic copolymer with reactive functionality distributed randomly throughout the polymer chain was prepared as follows: 150g of ethyl acetate was added into a 1L vessel equipped with a heating jacket, stirrer, feed tanks, and nitrogen gas inlet. The vessel was sealed under nitrogen atmosphere following three nitrogen-vacuum cycles to remove dissolved oxygen. The vessel was heated to 75 °C over a period of 30 min. A reagent mixture feed of 383.25g butyl acrylate (2.99mol), 1.75g acrylic acid (0.024mol), 1.5g DBTTC (5.16mmol), 0.2g Vazo 67 (1.04mmol), and 15g ethyl acetate was added over a period of 2 h. Over the 2 h reagent feed the contents were mixed at 100 rpm while maintaining a reaction temperature of 74-76 °C. The reaction conditions were maintained for an additional 3 h following completion of the reagent feed at which point > 90% of the monomer was consumed to generate an acrylic copolymer of theoretical \(M_n\) of 67,219 g/mol. The resulting solution polymer was then cooled to ambient temperature and discharged from the vessel.

Cross-linking of acrylic copolymer

100% based on moles of acrylic acid were targeted for cross-linking using PZ-28 cross-linker on equal molar equivalence. PZ-28 was diluted to 10 wt% concentration in ethyl acetate which was added into the acrylic copolymer solution with high speed mixing (≈1500 rpm) for 5
min. Unless noted otherwise, the adhesive composition was dried for 5 min at 120 ºC to eliminate the solvent, followed by 24 h at 65 ºC to ensure complete cross-linking. This polymer will be designated as PSA C from this point forward.

2.3.6 Polymerization of random, high molecular weight poly(butyl acrylate/acrylic acid)

A high molecular weight acrylic copolymer with reactive functionality distributed randomly throughout the polymer chain was prepared as follows: A 1L vessel equipped with a heating jacket, stirrer, feed tanks, and nitrogen gas inlet was sealed under nitrogen atmosphere following three nitrogen-vacuum cycles to removed dissolved oxygen. The heating jacket was heated to 69 ºC over a period of 30 min. A reagent mixture feed of 71.64g butyl acrylate, 0.36g acrylic acid, 0.14g Vazo 67, 1.08g isopropanol, and 106.92g ethyl acetate was added over a period of 20 min. Over the 20 min reagent feed the contents were mixed at 100 rpm while maintaining a reaction temperature of 68-70 ºC. The reaction conditions were maintained for an additional 40 min following completion of the reagent feed. A reagent mixture feed of 167.16g butyl acrylate, 0.84g acrylic acid, 0.34g Vazo 67, 2.52g isopropanol, and 249.48g ethyl acetate was then added over a period of 3 h. Over the 3 h reagent feed the contents were mixed at 100 rpm while maintaining a reaction temperature of 68-70 ºC. The reaction conditions were maintained for an additional 4 h following completion of the reagent feed. The resulting solution polymer was then cooled to ambient temperature and discharged from the vessel.

Cross-linking of acrylic copolymer

100% based on moles of acrylic acid were targeted for cross-linking using PZ-28 cross-linker on equal molar equivalence. PZ-28 was diluted to 10 wt% concentration in ethyl acetate
which was added into the acrylic copolymer solution with high speed mixing (~1500 rpm) for 5 min. Unless noted otherwise, the adhesive composition was dried for 5 min at 120 °C to eliminate the solvent, followed by 24 h at 65 °C to ensure complete cross-linking. This polymer will be designated as PSA D from this point forward.

2.3.7 Polymerization of triblock poly(methyl acrylate)-block-poly(butyl acrylate)-block-poly(methyl acrylate) using DBTTC as RAFT agent

An acrylic copolymer with a “hard” monomer positioned in the end-blocks was prepared as follows: 150g of ethyl acetate was added into a 1L vessel equipped with a heating jacket, stirrer, feed tanks, and nitrogen gas inlet. The vessel was sealed under nitrogen atmosphere following three nitrogen-vacuum cycles to remove dissolved oxygen. The vessel was heated to 75 °C over a period of 30 min. A reagent mixture feed of 85g methyl acrylate (0.99mol), 1.5g DBTTC (5.16mmol), and 0.2g Vazo 67 (1.04mmol) was added over a period of 60 min. Over the 60 min reagent feed the contents were mixed at 100 rpm while maintaining a reaction temperature of 74-76 °C. The reaction conditions were maintained for an additional 2 h following completion of the reagent feed at which point >90% of the monomer was consumed to generate end-blocks of theoretical $M_n$ of 7,406 g/mol. This polymer now becomes the macro-RAFT agent. A reagent mixture feed of 225g butyl acrylate (1.76mol), 0.2g Vazo 67 (1.04mmol), and 160g of ethyl acetate was then added over a period of 2 h. Over the 2 h reagent feed the contents were mixed at 100 rpm while maintaining a reaction temperature of 74-76 °C. The reaction conditions were maintained for an additional 3 h following completion of the reagent feed at which point > 90% of the monomer was consumed to generate a mid-block of theoretical $M_n$ of 35,292 g/mol. The resulting solution polymer was then cooled to ambient temperature and discharged from the vessel.
Drying of acrylic copolymer

Unless noted otherwise, this polymer was dried for 5 min at 120 °C. This polymer will be designated as PSA E from this point forward.

2.3.8 Polymerization of random poly(butyl acrylate/methyl acrylate) using DBTTC as RAFT agent.

An acrylic copolymer with a “hard” monomer distributed randomly throughout the polymer chain was prepared as follows: 150g of ethyl acetate was added into a 1L vessel equipped with a heating jacket, stirrer, feed tanks, and nitrogen gas inlet. The vessel was sealed under nitrogen atmosphere following three nitrogen-vacuum cycles to remove dissolved oxygen. The vessel was heated to 75 ºC over a period of 30 min. A reagent mixture feed of 225g butyl acrylate (1.76mol), 85g acrylic acid (0.99mol), 1.65g DBTTC (5.68mmol), 0.2g Vazo 67 (1.04mmol), and 160g ethyl acetate was added over a period of 2 h. Over the 2 h reagent feed the contents were mixed at 100 rpm while maintaining a reaction temperature of 74-76 ºC. The reaction conditions were maintained for an additional 3 h following completion of the reagent feed at which point > 90% of the monomer was consumed to generate an acrylic copolymer of theoretical $M_n$ of 52,006 g/mol. The resulting solution polymer was then cooled to ambient temperature and discharged from the vessel.

Drying of acrylic copolymer

Unless noted otherwise, this polymer was dried for 5 min at 120 °C. This polymer will be designated as PSA F from this point forward.
2.3.9 Polymerization of random, high molecular weight poly(butyl acrylate/methyl acrylate)

A high molecular weight acrylic copolymer with a “hard” monomer distributed randomly throughout the polymer chain was prepared as follows: A 1L vessel equipped with a heating jacket, stirrer, feed tanks, and nitrogen gas inlet was sealed under nitrogen atmosphere following three nitrogen-vacuum cycles to removed dissolved oxygen. The heating jacket was heated to 69 ºC over a period of 30 min. A reagent mixture feed of 52.2g butyl acrylate, 19.8g methyl acrylate, 0.14g Vazo 67, 1.08g isopropanol, and 106.92g ethyl acetate was added over a period of 20 min. Over the 20 min reagent feed the contents were mixed at 100 rpm while maintaining a reaction temperature of 68-70 ºC. The reaction conditions were maintained for an additional 40 min following completion of the reagent feed. A reagent mixture feed of 121.8g butyl acrylate, 46.2g methyl acrylate, 0.34g Vazo 67, 2.52g isopropanol, and 249.48g ethyl acetate was then added over a period of 3 h. Over the 3 h reagent feed the contents were mixed at 100 rpm while maintaining a reaction temperature of 68-70 ºC. The reaction conditions were maintained for an additional 4 h following completion of the reagent feed. The resulting solution polymer was then cooled to ambient temperature and discharged from the vessel.

Drying of acrylic copolymer

Unless noted otherwise, this polymer was dried for 5 min at 120 ºC.

This polymer will be designated as PSA G from this point forward.
RESULTS AND DISCUSSION

3.1 Butyl acrylate with CMDTTC

The aim of this study is to understand the influence of several experimental parameters on the RAFT homopolymerization of BA. The parameters of interest include:

- Ratio of $[\text{CMDTTC}]_0 / [\text{Vazo 67}]_0$;
- Ratio of $[\text{BA}]_0 / [\text{CMDTTC}]_0$;
- Reaction temperature.

Percent conversion was determined using GC/FID. Molecular weight and PDI were obtained by SEC. A general reaction scheme is shown below in Figure 14.

3.1.1 Influence of the $[\text{CMDTTC}]_0 / [\text{Vazo 67}]_0$ ratio

To investigate the influence of this parameter, four experiments (runs 1, 2, 3, and 4, respectively, in Table 1) were compared differing only by the ratio of $[\text{CMDTTC}]_0$ to $[\text{Vazo 67}]_0$, while keeping the ratio of $[\text{BA}]_0$ to $[\text{Vazo 67}]_0$ constant. As seen in Figure 15, $M_n(\text{sec})$ decreases with increasing CMDTTC concentration. With a $[\text{CMDTTC}]_0$ to $[\text{Vazo 67}]_0$ ratio of 3, 7.1, or 13.5, $M_n(\text{sec})$ values increase linearly with monomer conversion and are close to $M_n(\text{theoretical})$. The linearity of $M_n(\text{sec})$ vs. conversion indicates a constant number of propagating
chains and hence the lack of termination reactions, in good agreement with the theory of living polymerization. For a ratio of 3, $M_n(\text{sec})$ falls below $M_n(\text{theoretical})$ at high conversion ($\geq 90\%$). This may indicate the presence of irreversible chain termination due to monomer depletion. With a $[\text{CMDTTC}]_0$ to $[\text{Vazo 67}]_0$ ratio of 1.5, a loss of molecular weight control is observed. At high conversion ($> 40\%$), $M_n(\text{sec})$ values are lower than $M_n(\text{theoretical})$, indicating that the number of propagating chains produced at the onset of polymerization was greater than that predicted. On the other hand, irreversible chain termination may be another explanation as to why $M_n(\text{sec})$ deviates from $M_n(\text{theoretical})$. Irreversible chain termination most likely occurs by disproportionation. Disproportionation halts the propagation reaction when a free radical strips a hydrogen atom from an active polymer chain. The abstracted polymer chain will then form a carbon-carbon double bond at its end.

As seen in Figure 16, increasing the ratio of $[\text{CMDTTC}]_0$ to $[\text{Vazo 67}]_0$ also influences PDI. With a $[\text{CMDTTC}]_0$ to $[\text{Vazo 67}]_0$ ratio of 7.1, or 13.5, PDI decreases with conversion, in good agreement with the theory of living polymerization. During the beginning of a RAFT polymerization, PDI is dictated by conventional free radical polymerization, giving rise to a high PDI. As the polymerization proceeds, RAFT-mediated chain equilibration is established, control over molecular weight occurs and a decrease in PDI is expected. For a $[\text{CMDTTC}]_0$ to $[\text{Vazo 67}]_0$ ratio of 1.5 or 3, an increase in PDI is observed at high conversion; greater than 40\% and 90\%, respectively. This further indicates the presence of irreversible chain termination at these specific ratios.
Figure 15: $M_n$ vs. conversion for BA polymerizations with Vazo 67 as initiator and CMDTTC as RAFT agent.

Figure 16: PDI vs. conversion for BA polymerizations with Vazo 67 as initiator and CMDTTC as RAFT agent.
From this set of experiments it can be concluded that:

- $M_n(\text{sec})$ decreases with increasing CMDTTC concentration;

- An appropriate $[\text{CMDTTC}]_0$ to $[\text{Vazo 67}]_0$ ratio for the combination of BA and CMDTTC, from the tested ratios, is at least 3.0. For all ratios greater than or equal to 3.0, $M_n(\text{sec})$ values are close to $M_n(\text{theoretical})$ and a low PDI is observed throughout the entire polymerization.

3.1.2. Influence of the $[\text{BA}]_0 / [\text{CMDTTC}]_0$ ratio

According to equation 1, when $M_n(\text{theoretical})$ is to be changed, the ratio of $[M]_0$ to $[\text{RAFT}]_0$ must be modified. To investigate the influence of this parameter, four experiments (runs 5, 6, 7, and 8, respectively, in Table 2) were compared differing only by the ratio of $[\text{BA}]_0$ to $[\text{CMDTTC}]_0$, while keeping the ratio of $[\text{CMDTTC}]_0$ to $[\text{Vazo 67}]_0$ constant. A $[\text{CMDTTC}]_0$ to $[\text{Vazo 67}]_0$ ratio of 4.5 was selected based on results from section 3.1.1. As seen in Figure 17, increasing the ratio of $[\text{BA}]_0$ to $[\text{CMDTTC}]_0$ from 330.2 to 660.4 resulted in a linear increase in $M_n(\text{sec})$ from 41,308 to 78,789 g/mol. It should also be noted that the slope of the plot in Figure 16 (120.49 g/mol) is quite close to the monomer molecular weight of BA (128.17 g/mol); indicating the validity of equation 1. All four polymers were also characterized by a PDI < 1.5. This fully confirms that the four polymers were synthesized via a controlled mechanism.

Excellent control over molecular weight is also observed. As seen in Figure 18, the $M_n(\text{sec})$ values are quite close to $M_n(\text{theoretical})$ for all four ratios of $[\text{BA}]_0$ to $[\text{CMDTTC}]_0$. 

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Figure 17: Effect of $[BA]_0 / [CMDTTC]_0$ on $M_n$ and PDI.

Figure 18: Effect of $[BA]_0 / [CMDTTC]_0$ on $M_n$ control.
Increasing the ratio of [BA]₀ to [CMDTTC]₀ also induces a slight decrease in conversion (Figure 19). The polymerization rate remains satisfactory when the [BA]₀ to [CMDTTC]₀ ratio is increased to 410.4 (with more than 90% conversion obtained in 5 h). With a higher ratio of 495.3 or 660.4, greater than 5 h are needed to reach the same conversion. However, the possibility of irreversible chain termination may increase if time is added to the polymerization.

![Figure 19: Effect of [BA]₀ / [CMDTTC]₀ on % conversion at time = 5 h.](image)

From this set of experiments it can be concluded that:

- A higher initial [BA]₀ to [CMDTTC]₀ ratio results in higher molecular weights but conversions are lower in the same period of reaction time;
- Reducing the [BA]₀ to [CMDTTC]₀ ratio induces a slight improvement of the molecular weight control;
- PDI appears not to be influenced by increasing the ratio of [BA]₀ to [CMDTTC]₀.
3.1.3 Influence of temperature

Butyl acrylate polymerization, in the presence of CMDTTC, was investigated at three different polymerization temperatures, namely 65, 75, and 85 °C (runs 9, 10, and 11, respectively, in Table 3). At 65 °C butyl acrylate polymerization only reaches 78% conversion in 5 h. At 75 and 85 °C, 90% conversion is obtained in 4 h and 3 h, respectively (Figure 20). Conversion increases with higher temperatures due to the increasing kinetic parameters.

![Figure 20: Kinetics of BA polymerizations at 65, 75, and 85 °C in the presence of Vazo 67 as initiator and CMDTTC as RAFT agent.](image)

Concerning the control of molecular weight, the use of CMDTTC affords suitable results (Figure 21). Independent of the reaction temperature, $M_{n(\text{sec})}$ increased linearly with monomer conversion, in good agreement with the theory of living polymerization. At 75 and 85 °C, the
slope of the curve is no longer linear above 80% conversion. This behavior suggests the presence of irreversible chain termination (i.e., disproportionation) due to monomer depletion.

Independent of the reaction temperature, PDI remained below 2.0 throughout the polymerization (Figure 22). These results also confirm that the polymerizations proceeded via a controlled mechanism. However, at 75 and 85 ºC, the PDI begins to increase at high monomer conversions (> 80%). This further confirms the presence of irreversible chain termination.
The appropriate reaction temperature for the combination of BA and CMDTTC, from the tested temperatures, is 75 °C. It gives the best balance between the following parameters:

- Fast kinetics to a given conversion;
- Good control of polymerization, resulting in low PDIs;
- Strong correlation between $M_n(\text{sec})$ and $M_n(\text{theoretical})$. 

Figure 22: PDI vs. conversion of BA polymerizations at 65, 75, and 85 °C in the presence of Vazo 67 as initiator and CMDTTC as RAFT agent.
3.2 Butyl acrylate with DBTTC

The aim of this study is to understand the influence of several experimental parameters on the RAFT homopolymerization of BA. The parameters of interest include:

- Ratio of \([\text{DBTTC}]_0 / [\text{Vazo 67}]_0\);
- Ratio of \([\text{BA}]_0 / [\text{DBTTC}]_0\);
- Reaction temperature.

Percent conversion was determined using GC/FID. Molecular weight and PDI were obtained by SEC. A general reaction scheme is shown below in Figure 23.

![Reaction scheme for RAFT polymerization of butyl acrylate, mediated by DBTTC.](image)

Figure 23: Reaction scheme for RAFT polymerization of butyl acrylate, mediated by DBTTC.

3.2.1 Influence of the \([\text{DBTTC}]_0 / [\text{Vazo 67}]_0\) ratio

To investigate the influence of this parameter, four experiments (runs 12, 13, 14, and 15, respectively, in Table 4) were compared differing only by the ratio of \([\text{DBTTC}]_0\) to \([\text{Vazo 67}]_0\), while keeping the ratio of \([\text{BA}]_0\) to \([\text{Vazo 67}]_0\) constant. As seen in Figure 24, \(M_{n(\text{sec})}\) decreases with increasing DBTTC concentration. With a \([\text{DBTTC}]_0\) to \([\text{Vazo 67}]_0\) ratio of 4.9, 7.4, or 10.7, \(M_{n(\text{sec})}\) values increase linearly with monomer conversion and are close to \(M_{n(\text{theoretical})}\). The linearity of \(M_{n(\text{sec})}\) vs. conversion indicates a constant number of propagating chains and hence
the lack of termination reactions, in good agreement with the theory of living polymerization. With a [DBTTC]₀ to [Vazo 67]₀ ratio of 1.1, a loss of molecular weight control is observed. At high conversion (> 60%), \(M_n(\text{sec})\) values are lower than \(M_n(\text{theoretical})\), indicating that the number of propagating chains produced at the onset of polymerization was greater than that predicted. On the other hand, irreversible chain termination (i.e., disproportionation) may be another explanation as to why \(M_n(\text{sec})\) deviates from \(M_n(\text{theoretical})\).

As seen in Figure 25, increasing the ratio of [DBTTC]₀ to [Vazo 67]₀ also influences PDI. With a [DBTTC]₀ to [Vazo 67]₀ ratio of 4.9, 7.4, or 10.7, PDI decreases with conversion, in good agreement with the theory of living polymerization. As stated earlier, during the beginning of a RAFT polymerization, PDI is dictated by conventional free radical polymerization, giving rise to a high PDI. As the polymerization proceeds, RAFT-mediated chain equilibration is established, control over molecular weight occurs and a decrease in PDI is expected. For a [DBTTC]₀ to [Vazo 67]₀ ratio of 1.1, an increase in PDI is observed at high conversion (> 60%), further indicating the presence of irreversible chain termination.
Figure 24: $M_n$ vs. conversion for BA polymerizations with Vazo 67 as initiator and DBTTC as RAFT agent.

Figure 25: PDI vs. conversion for BA polymerizations with Vazo 67 as initiator and DBTTC as RAFT agent.
From this set of experiments it can be concluded that:

- \( M_n(\text{sec}) \) decreases with increasing DBTTC concentration;
- An appropriate \([\text{DBTTC}]_0\) to \([\text{Vazo 67}]_0\) ratio for the combination of BA and DBTTC, from the tested ratios, is at least 4.9. For all ratios greater than or equal to 4.9, \( M_n(\text{sec}) \) values are close to \( M_n(\text{theoretical}) \) and a low PDI is observed throughout the entire polymerization.

### 3.2.2 Influence of the \([\text{BA}]_0 / [\text{DBTTC}]_0\) ratio

According to equation 1, when \( M_n(\text{theoretical}) \) is to be changed, the ratio of \([\text{M}]_0\) to \([\text{RAFT}]_0\) must be modified. To investigate the influence of this parameter, four experiments (runs 16, 17, 18, and 19, respectively, in Table 5) were compared differing only by the ratio of \([\text{BA}]_0\) to \([\text{DBTTC}]_0\), while keeping the ratio of \([\text{DBTTC}]_0\) to \([\text{Vazo 67}]_0\) constant. A \([\text{DBTTC}]_0\) to \([\text{Vazo 67}]_0\) ratio of 4.9 was selected based on results from section 3.2.1. As seen in Figure 26, increasing the ratio of \([\text{BA}]_0\) to \([\text{DBTTC}]_0\) from 301.7 to 679.6 resulted in a linear increase in \( M_n(\text{sec}) \) from 36,085 to 73,300 g/mol. It should also be noted that the slope of the plot in Figure 25 (110.37 g/mol) is quite close to the monomer molecular weight of BA (128.17 g/mol); indicating the validity of equation 1. All four polymers were also characterized by a PDI < 1.5. This fully confirms that the four polymers were synthesized via a controlled mechanism.

Excellent control over molecular weight is also observed. As seen in Figure 27, the \( M_n(\text{sec}) \) values are quite close to \( M_n(\text{theoretical}) \) for all four ratios of \([\text{BA}]_0\) to \([\text{DBTTC}]_0\).
Figure 26: Effect of $[\text{BA}]_0 / [\text{DBTTC}]_0$ on $M_n$ and PDI.

Figure 27: Effect of $[\text{BA}]_0 / [\text{DBTTC}]_0$ on $M_n$ control.
Increasing the ratio of $[BA]_0$ to $[DBTTC]_0$ also induces a slight decrease in conversion (Figure 28). The polymerization rate remains satisfactory when the $[BA]_0$ to $[CMDTTCC]_0$ ratio is 301.7 (with more than 90% conversion obtained in 5 h). However, with a higher ratio of 452.6, 603.4, or 679.6, greater than 5 h are needed to reach the same conversion. Once again, the possibility of irreversible chain termination may increase if time is added to the polymerization.

![Figure 28: Effect of $[BA]_0$ / $[DBTTC]_0$ on % conversion at time = 5 h.](image)

From this set of experiments it can be concluded that:

- A higher initial $[BA]_0$ to $[DBTTC]_0$ ratio results in higher molecular weights but conversions are lower in the same period of time;
- Reducing the $[BA]_0$ to $[DBTTC]_0$ ratio induces a slight improvement of the molecular weight control;
- PDI appears not to be influenced by increasing the ratio of $[BA]_0$ to $[DBTTC]_0$. 

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3.2.3 Influence of temperature

Butyl acrylate polymerization, in the presence of DBTTC, was investigated at three different polymerization temperatures, namely 65, 75, and 85 °C (runs 20, 21, and 22, respectively, in Table 6) (Figure 29). At 65 °C butyl acrylate polymerization in the presence of DBTTC only reaches 70% conversion in 5 h. A 1 h inhibition period is also observed at 65 °C (i.e., no polymerization activity has taken place). Based on the mechanism shown in Figure 8, several explanations for inhibition are plausible. They include the following:

- Slow fragmentation of the radical intermediate (2) formed from the initial RAFT agent (1);
- Slow fragmentation of the radical intermediate (4) formed from the polymeric RAFT agent (3);
- Slow reinitiation by the expelled radical (R·).

At 75 and 85 °C, 90% conversion is obtained in 5 h and 4 h, respectively. Once again, conversion increases with higher temperatures due to the increasing kinetic parameters.
Concerning the control of molecular weight, the use of DBTTC affords suitable results. Independent of the reaction temperature, $M_n$ increased linearly with monomer conversion (Figure 30), in good agreement with the theory of living polymerization. As seen in Figure 29, a 1 h inhibition period is present at 65 °C. The data in Figure 30 shows that the inhibition period had no effect on the molecular weight control; $M_{n(sec)}$ still increased linearly with monomer conversion.

When compared to CMDTTC (Figure 21), the $M_{n(sec)}$ of DBTTC continued to increase linearly at high conversion (> 80%). Based on the mechanism shown in Figure 8, the difference can be attributed to the equilibrium between dormant and active species during the “main equilibrium” step. A faster equilibrium between the two species will reduce the amount of irreversible chain termination reactions. On the other hand, a faster equilibrium between the two species will reduce % conversion at the conclusion of polymerization. This theory holds true.
because for all three polymerization temperatures the % conversion of BA after 5 h is lower in the presence of DBTCC relative to CMDTTC.

Figure 30: $M_n$ vs. conversion of BA polymerizations at 65, 75, and 85 ºC in the presence of Vazo 67 as initiator and DBTT as RAFT agent.

At 65 and 75 ºC, PDI decreases with conversion to reach very low values (Figure 31). These results also confirm that the polymerizations proceeded via a controlled mechanism. At 85 ºC, the PDI decreases with conversion to reach a very low value (1.416 at 80% conversion). Then, above 80% conversion, PDI begins to increase, because, the probability of irreversible chain termination increases when monomer concentration decreases.
The appropriate reaction temperature for the combination of BA and DBTTC, from the tested temperatures, is 75 °C. It gives the best balance between the following parameters:

- Fast kinetics to a given conversion;
- Good control of polymerization, resulting in low PDIs;
- Strong correlation between $M_n(\text{exp})$ and $M_n(\text{theoretical})$.
3.3 Effects of controlled monomer placement

It is well known that an inverse relationship usually exists between changes in adhesive and cohesive strength for a PSA: loss of adhesion usually provides an improvement in cohesive strength and vice versa. Therefore, significantly improving both adhesion and cohesion strengths for a PSA is a very tough challenge. One potential way to break this paradigm is to control cross-link density (i.e., MW between cross-links) through the use of block copolymers.

3.3.1 BA/AA triblock copolymers vs. random copolymers

In order to improve tack and peel strength, without sacrificing shear strength, triblock copolymers of BA/AA were polymerized. Table 7 describes the various polymers used with regards to molecular weight, % solids, and solution viscosity. Copolymers of BA and AA at the same weight ratios were polymerized using RAFT and conventional free radical polymerization to provide four distinct architectures. The first column, labeled A, is a low molecular weight, low PDI triblock copolymer in which the acid groups have been positioned into the mid-block of the polymer. The second column, labeled B, is another low molecular weight, low PDI triblock copolymer in which the acid groups have been positioned into the end-blocks of the polymer. The third column, labeled C, is a low molecular weight, low PDI random copolymer in which the acid groups have been randomly distributed throughout the entire polymer. Polymers A, B, and C were all polymerized via RAFT polymerization. The fourth column, labeled D, is a high molecular weight, high PDI random copolymer in which the acid groups have been randomly distributed throughout the entire polymer. Polymer D was polymerized via conventional free radical polymerization.
Table 7: Test results of PSAs A, B, C, and D with regards to MW, % solids, and solution viscosity.

The RAFT examples display solids content in excess of 65% with viscosities at approximately 1,000 – 5,000 cps. By contrast, the polymer prepared by conventional free radical polymerization displays a viscosity of approximately 5,000 cps when diluted to a solids content of 38%.

Based on the DSC thermograms (Figure 32), all four PSAs display an identical transition at approximately -44 °C which indicates that they are all equal in $T_g$. 
Upon drying and cross-linking, DMA and physical testing was performed to understand the differences in viscoelastic properties and physical performance, respectively.

In Figure 33, G’ and tan δ versus frequencies from 0.01 to 628 rad/sec is plotted. The G’ and tan δ at 0.01 rad/sec correlates to the shear strength (i.e., cohesive strength) of a PSA.³ PSAs B, C, and D show a similar G’ and tan δ at low frequency. Therefore, when reactive functionality is placed into the end-blocks of a triblock copolymer, its cohesive strength is comparable to a random copolymer. Meanwhile, PSA A exhibits a significantly lower G’ and higher tan δ at 0.01 rad/sec. These results indicate that PSA A has lower cohesive strength which translates into lower shear strength. Therefore, when reactive functionality is placed into the mid-block of a triblock copolymer, its cohesive strength is no longer comparable to a random
copolymer. The difference can be attributed to the PSA possessing two free blocks of mobile polymer. The rheological behavior correlates well with the experimental shear strength data listed in Table 8. PSA B, C, and D withstood a 500g load for greater than 6,000 h. PSA A only hung for approximately 400 min and a split-transfer failure mode was generated.

Figure 33: G’ and tan δ vs. frequency for PSAs A, B, C, and D.
Table 8: Shear Strength data for PSAs A, B, C, and D.

<table>
<thead>
<tr>
<th>Shear (failure time, min)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
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<tr>
<td></td>
<td>415.4</td>
<td>&gt; 6,000</td>
<td>&gt; 6,000</td>
<td>&gt; 6,000</td>
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Adhesive bond formation depends on two factors: material bulk properties (*i.e.*, viscoelastic properties) and surface forces. Surface forces include surface tension and specific inter-molecular interactions such as hydrogen bonding, covalent bonding, and ionic bonding. For this particular study, any contribution to the adhesive bond formation from surface forces will not be accounted for because all four PSAs are identical in chemical composition. On the other hand, viscoelastic properties are closely associated with rheological behavior. Therefore, this study will focus on the rheological behavior of the PSA and how it correlates to peel adhesion.

Peel adhesion involves both bond formation (bonding) and bond breaking (debonding). The bond formation correlates to the loss modulus (*G''*) at low frequency. In other words, the higher the *G''* value at 0.01 rad/sec, the more favorable is the bonding. PSAs A and B exhibit a significantly higher *G''* at low frequency (Figure 34). A higher *G''* at 0.01 rad/sec indicates better flow-out ability and good wetting. The significant difference in performance can be attributed to the free mobile polymer located in the end-blocks or mid-block, respectively. The debonding strength comes from two contributing terms: the cohesive strength which is indicated by *G’*, and the energy of dissipation which is indicated by *G’'*, both measured at a frequency of 100 rad/sec. High cohesive strength and excessive energy dissipation leads to a high peel value. As seen in Figures 33 and 34, respectively, more energy is required to peel off PSA A than PSA B simply because the former has a higher *G’* and *G’'* at the debonding frequency. The difference can be attributed to PSA A possessing two free blocks of mobile polymer instead of one. PSAs
C and D exhibit an even lower G’ and G” at 100 rad/sec. This indicates that less energy is required to remove these two. Therefore, it is predicted that both random copolymers will exhibit a substantial decrease in peel adhesion. The rheological behavior correlates very well with the experimental peel data listed in Figures 35 and 36, respectively. The 15 min and 24 h, 180° peel values of these four PSAs on SS and HDPE panels follow the same trend as the rheological data.
Figure 34: $G''$ vs. frequency for PSAs A, B, C, and D.
Figure 35: 15 min and 24 h peel strength to SS data for PSAs A, B, C, and D.

Figure 36: 15 min and 24 h peel strength to HDPE data for PSAs A, B, C, and D.
The correlation of tack performance is similar to that of peel, except the bonding frequency for tack is about 1.0 rad/sec. How well the PSA can wet out onto the surface and how much cohesive strength needed to hold the bond are both critical in controlling tack performance. Once again, PSAs A and B exhibit a substantially higher G” at 1.0 rad/sec (Figure 34). A higher G” at the bonding frequency indicates increased amounts of wetting. As mentioned before, the significant difference in performance can be attributed to the free mobile polymer located in the end-blocks or mid-block, respectively. The results of G’ and G” at 100 rad/sec were already discussed above. In summary, PSA A had the highest values, followed by PSAs B, C, and D, respectively. Based on their rheological behavior, it can be predicted that PSA A has the highest degree of tack, followed by PSAs B, C, and D, respectively. The rheological behavior correlates with the experimental probe tack data listed in Figure 37. A similar trend is observed at both 1.0 and 10.0 sec dwell times. A dwell time of 10.0 sec generates a higher tack value due to the increase in contact time against the probe.

![Figure 37: Probe tack data for PSAs A, B, C, and D. A dwell time of 1 and 10 sec, respectively, was used.](image-url)
Another way to analyze rheological behavior is to test versus temperature instead of frequency. Figure 38 is a plot of $G'$ and $\tan \delta$ as a function of temperature for the four PSAs described in Table 7. All of the polymers display an identical $T_g$ at approximately -35 ºC (Note: A 10 ºC offset is seen between DSC and DMA. This is typical and can be attributed to a difference in ramp rate). At temperatures greater than the $T_g$ the polymers begin to differ substantially. For example, PSA A displays a significantly lower $G'$. This indicates that PSA A is more viscous and lacks cohesive strength. This result correlates to the shear strength, peel strength, and tack data outlined above. Another observation is the significant difference in the $\tan \delta$ profiles. PSA D displays extremely low $\tan \delta$ values which are indicative of a higher molecular weight and consequently higher modulus (i.e., stiffer) material. PSA C has $\tan \delta$ values equivalent to that of PSA D at approximately 50 ºC indicating equivalence in cross-link density. In contrast, the $\tan \delta$ values of PSA A and B remain higher up to 135 ºC and 115 ºC, respectively. This is indicative of higher molecular weight between cross-links brought upon by the change in architecture.
Figure 38: G’ and tan δ vs. temperature for PSAs A, B, C, and D.

From this set of experiments it can be concluded that:

- Free mobile uncross-linked polymer segments located throughout the polymer chain does indeed increase peel adhesion and tack relative to random copolymers;
- However, shear strengths are only comparable to random copolymers when the free mobile polymer is located in the mid-block.
3.3.2 BA/MA triblock copolymers vs. random copolymers

In order to improve shear strength, without sacrificing tack and peel strength, a triblock copolymer of BA/MA was polymerized in which the MA was strategically positioned into the end-block. Table 9 describes the various polymers used with regards to molecular weight, % solids, and solution viscosity. Copolymers of BA and MA at the same weight ratios were polymerized using RAFT and conventional free radical polymerization to provide three distinct architectures. The first column, labeled E, is a low molecular weight, low PDI triblock copolymer in which MA has been positioned into the end-blocks and BA has been positioned into the mid-block, respectively. The second column, labeled F, is another low molecular weight, low PDI random copolymer in which MA and BA have been randomly distributed throughout the entire polymer. Polymers E and F were polymerized via RAFT polymerization. The third column, labeled G, is a high molecular weight, high PDI random copolymer in which MA and BA has been randomly distributed throughout the entire polymer. Polymer G was polymerized via conventional free radical polymerization.

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_n$(end block)</td>
<td>6,910</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>$M_w$(end block)</td>
<td>10,956</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>$M_n$(mid block)</td>
<td>30,856</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>$M_w$(mid block)</td>
<td>55,362</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>$M_n$(polymer)</td>
<td>44,676</td>
<td>38,551</td>
<td>75,736</td>
</tr>
<tr>
<td>$M_w$(polymer)</td>
<td>77,274</td>
<td>54,427</td>
<td>238,587</td>
</tr>
<tr>
<td>PDI</td>
<td>1.730</td>
<td>1.412</td>
<td>3.151</td>
</tr>
<tr>
<td>% Solids</td>
<td>47.96</td>
<td>45.48</td>
<td>37.52</td>
</tr>
<tr>
<td>Viscosity</td>
<td>600 cps</td>
<td>200 cps</td>
<td>12,500 cps</td>
</tr>
</tbody>
</table>

Table 9: Test results of PSAs E, F, and G with regards to MW, % solids, and solution viscosity.
The RAFT examples display solids content in excess of 45% with viscosities at approximately 200 – 600 cps. By contrast, the polymer prepared by conventional free radical polymerization displays a viscosity of approximately 12,500 cps when diluted to a solids content of approximately 38%.

Based on the DSC thermograms (Figure 39), PSAs F and G exhibit a single transition at approximately -27 ºC. This indicates that they are equal in $T_g$. PSA E exhibits two separate and distinct $T_g$s at approximately -44 ºC and 8 ºC, respectively. Two $T_g$s are present due to the microphase separation of the MA end-blocks from the BA mid-block.

![Figure 39: DSC thermograms of PSAs E, F, and G.](image-url)
In Figure 40, $G'$ and $\tan \delta$ versus frequencies from 0.01 to 628 rad/sec is plotted. As mentioned before, $G'$ and $\tan \delta$ at 0.01 rad/sec correlates to shear strength of a PSA. PSA E exhibits a higher $G'$ and lower $\tan \delta$ at low frequency. Thus, it’s predicted that the shear strength of PSA E is greater than PSA G. The rheological behavior correlates well with the experimental shear data in Table 10. PSA E withstood a 500g load for approximately 85 min while PSA G only hung for approximately 12 minutes. Both PSAs also exhibited a failure mode of split-transfer. The increase in shear strength can be attributed to the presence of physical cross-linking sites. This is due to the microphase separation of the BA mid-block from the MA end-blocks, respectively. The shear strength of PSA F was not tested due to its significantly lower $G'$ and extremely high $\tan \delta$ value at 0.01 rad/sec. This is due to the low molecular weight of the PSA.
Figure 40: $G'$ and tan $\delta$ vs. frequency for PSAs E, F, and G.

<table>
<thead>
<tr>
<th></th>
<th>E</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shear (failure time, min)</td>
<td>85</td>
<td>12</td>
</tr>
<tr>
<td>Failure Mode</td>
<td>st</td>
<td>st</td>
</tr>
</tbody>
</table>

Table 10: Shear strength data for PSAs E and G.
As mentioned before, adhesive bond formation depends on two factors: material bulk properties (i.e., viscoelastic properties) and surface forces. Once again, surface forces will not be accounted for because all three PSAs are identical in chemical composition.

The bonding efficiency can be correlated to the $G''$ at low frequency. In other words, the higher the $G''$ value at 0.01 rad/sec, the more favorable is the bonding. As seen in Figure 41, PSA E exhibits a slightly higher $G''$ at 0.01 rad/sec relative to PSA G. A higher $G''$ at low frequency indicates better flow-out ability and good wetting. However, as seen in Figures 42 and 43, respectively, the rheological data does not correlate to the peel strength data. After 15 min, the peel strength is higher to both SS and HDPE for PSA G. Therefore, the peel data indicates that PSA G has better flow-out ability and wetting. From further inspection of the data, the answer appears to correlate to the tan $\delta$ at 0.01 rad/sec. As seen in Figure 40, the tan $\delta$ of PSA G is substantially higher than PSA E at low frequency. Therefore, as tan $\delta$ increases the viscous component begins to dominate. This would appear to explain the difference in peel strength after 15 min.

As mentioned above, the debonding strength comes from two contributing terms: the cohesive strength which is indicated by $G'$, and the energy of dissipation which is indicated by $G''$, both measured at a frequency of 100 rad/sec. High cohesive strength and excessive energy dissipation leads to a high peel value. As seen in Figures 40 and 41, respectively, more energy is required to peel off PSA E than PSA G because the former has a higher $G'$ and $G''$ at the debonding frequency. However, once again, the rheological data does not correlate to the peel strength data in Figures 42 and 43, respectively. After 24 h, the peel strength to SS are similar for both PSAs. From further inspection of the data, the answer once again appears to correlate to the tan $\delta$ at 100 rad/sec. As seen in Figure 40, the tan $\delta$ of both PSAs is almost identical.
Therefore, the amount of elastic and viscous component each PSA possesses is similar. Thus, a similar peel value would be expected. After 24 h, the peel strength to HDPE is still significantly greater for PSA G. When bonding to low surface energy substrates the amount of viscous component a PSA possess is even more critical. Therefore, the higher tan δ of PSA G at 0.01 rad/sec is the reason for the dramatic difference in peel strengths to HDPE.

Overall, the presence of physical cross-linking from the MA end-blocks has increased the G’ of PSA E across the entire frequency range relative to PSA G. Literature\textsuperscript{4} indicates that a PSA exhibits good performance when G’ is low at low frequencies and there is a high slope for G’ as the frequency increases. PSAs with higher G’ will possess better cohesive strength, however, if G’ becomes too high the adhesive may not wet the surface initially. On the other hand, the free block of mobile BA helps to improve polymer flow over time thus generating similar peel strengths to polar surfaces.

The peel strength of PSA F was not tested due to its significantly lower G’ and extremely high tan δ value at 0.01 rad/sec. This is due to the low molecular weight of the PSA.
Figure 41: $G''$ vs. frequency for PSAs E, F, and G.
Figure 42: 15 min and 24 h peel strength to SS data for PSAs E and G.

Figure 43: 15 min and 24 h peel strength to HDPE data for PSAs E and G.
Because it was determined above that tan $\delta$ correlates better to peel strength data, it will also be used to characterize tack. As seen in Figure 40, the tan $\delta$ at 1.0 and 100 rad/sec, respectively, are quite similar. Thus, it can be predicted that both PSAs should exhibit similar tack. The rheological behavior correlates with the experimental probe tack data listed in Figure 44. The data indicates that both PSAs exhibit similar probe tack at both 1 and 10 sec dwell time, respectively. Once again, a dwell time of 10.0 sec generates a higher tack value due to the increase in contact time against the probe.

![Figure 44: Probe tack data for PSAs E and G. A dwell time of 1 and 10 sec, respectively, was used.](image)

Figure 45 is a plot of $G'$ and tan $\delta$ as a function of temperature for the three PSAs described in Table 9. PSAs F and G display an identical $T_g$ at approximately -15 °C. PSA E exhibits two separate and distinct $T_g$s at approximately -32 °C and 17 °C, respectively (Note: A 10 °C offset is seen between DSC and DMA. This is typical and can be attributed to a difference in ramp rate). As mentioned before, two $T_g$s are present due to the microphase separation of the
MA end-blocks from the BA mid-block. On continued heating the melting point of each polymer differs substantially. The melting point is where the free volume has increased so that the polymer chains can slide past each other and the material flows. The ability to flow is determined as the temperature at which tan δ is greater than one. PSA F exhibits substantially higher tan δ values at all temperatures above the Tg. This PSA appears to melt as soon as it passes through its Tg. This behavior is due to the exceptionally low molecular weight of the random copolymer. Significantly lower tan δ values are observed for PSA G. This PSA does not appear to melt until approximately 90 °C. The increase in the melt flow temperature can be attributed to the increase in molecular weight of the random copolymer. In contrast, PSA E exhibits a much different tan δ profile. The tan δ values remain quite low and never approach one at all temperatures above the Tg. This indicates that the PSA possesses no melt flow. This phenomenon can be attributed to the MA end-blocks associating to form small morphological domains that serve as physical cross-linking and reinforcement sites. Therefore, a PSA that is cross-linked will not melt as it is unable to flow. On the other hand, PSA E should flow once the MA domains are dissociated. Based on the rheological data the dissociation temperature of MA is greater than 200 °C. Unlike PSAs F and G, the G’ of PSA E remained relatively flat above its Tg. This is also indicative of a cross-linked PSA.
Figure 45: $G'$ and $\tan\delta$ vs. temperature for PSAs E, F, and G.

From this set of experiment it can be concluded that:

- Physical cross-linking of the MA end-blocks has increased the shear strength of a non-functional PSA when compared to a random control;
- The peel strength and tack are still comparable to a random control.
CONCLUSIONS

The RAFT polymerization of BA has been studied in detail, in the presence of CMDTTC and DBTTC. The influence of several experimental parameters, such as CTA to initiator molar ratio, BA to CTA molar ratio, and temperature were investigated in order to determine the conditions leading to optimal control (in terms of polymerization time, MW, and PDI). Similar trends were observed for both CTAs. Kinetics appear strongly influenced by the polymerization temperature, and to a lesser extent BA concentration. An increase in the molar ratio of [CTA] / [Vazo 67] resulted in a decrease in MW. Comparison of the data also suggests the existence of an optimal [CTA] / [Vazo 67] ratio; greater than or equal to 3.0 and 4.9 for CMDTTC and DBTTC, respectively. At these ratios excellent MW control and low PDI were observed throughout the entire polymerization. An increase in [BA] / [CTA] generated a linear increase in MW. Once again, excellent MW control and low PDI were observed for each ratio. Independent of the reaction temperature, $M_n$ increased linearly and PDI decreased with monomer conversion. For CMDTTC at 75 and 85 ºC, the slope of the curve is no longer liner above 80% conversion. This can be attributed to the slow equilibrium between active and dormant species during the “main equilibrium” step of RAFT polymerization.

The PSA performance and viscoelastic properties of random copolymers were compared to block copolymers of the same acrylic composition. Random copolymers and block copolymers were polymerized by conventional free radical and RAFT polymerization, respectively. Triblock copolymers of BA/AA were polymerized in which the AA was positioned into the end-blocks or mid-block, respectively. When compared to random copolymers of the same acrylic composition, both triblock copolymers exhibited higher peel adhesion and tack.
However, only the triblock copolymer in which the AA was positioned into the end-blocks gave comparable shear strength.

A triblock copolymer of BA/MA was also polymerized in which the MA was strategically positioned into the end-blocks. When compared to random copolymers of the same acrylic composition, the triblock copolymer exhibited similar peel adhesion and tack. In addition, the triblock copolymer had higher shear strength. The increase in shear strength can be attributed to the presence of physical cross-linking sites. This is due to the microphase separation of the BA mid-block from the MA end-blocks, respectively. The triblock copolymer of BA/MA also exhibited no melt flow up to 200 °C.
REFERENCES


