Controlling the Morphology of Dynamic Thia-Michael Networks to Target Pressure-Sensitive and Hot Melt Adhesives

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ABSTRACT: A series of multistage (pressure-sensitive/hot melt) adhesives utilizing dynamic thia-Michael bonding motifs are reported. The benzalcyanoacetate Michael acceptors used in this work undergo bond exchange under ambient conditions without external catalysis, facilitating pressure-sensitive adhesion. A key feature of this system is the dynamic reaction-induced phase separation that lends reinforcement to the otherwise weakly bonded materials, enabling weak, repeatable pressure-sensitive adhesion under ambient conditions and strong adhesion when processed as a hot melt adhesive. By using different pairs of benzalcyanoacetate cross-linking units, the phase separation characteristics of the adhesives can be directly manipulated, allowing for a tailored adhesive response.

KEYWORDS: dynamic covalent chemistry, pressure sensitive adhesive, hot melt adhesive, phase separation, rheology, thia-Michael bonds

INTRODUCTION

The scope of adhesive materials in daily life spans a vast range of targeted applications. From the biomedical to infrastructure sectors, modern adhesives are highly engineered to enable further functions that include conductivity,5−7 biocompatibility,8−11 degradability,8−11 and smart adhesion.12−14 In addition, these materials are traditionally subject to a range of mechanical property requirements depending on their desired purpose. For instance, pressure-sensitive adhesives (PSAs), such as those on the back of sticky notes or adhesive tapes,15,16 require soft, viscoelastic solids for fast adhesion. Conversely, a hot melt adhesive (HMA) like a hot glue is designed to withstand large loads17 and therefore necessitates the use of materials with high mechanical strength at typical operating temperatures. This expansive array of material requirements presents an intriguing opportunity to design new multipurpose adhesives that can be used in both pressure-sensitive and structural adhesive applications.

Recently, the integration of dynamic or reversible bonds into adhesive systems has shown considerable promise in developing a new generation of adhesive materials.18−27 With applications ranging from underwater PSAs to rebondable structural adhesives, the dynamic bonds’ ability to continuously break and reform in response to a stimulus without unwanted, irreversible side reactions28−31 provides a means through which critical adhesion properties (i.e., surface wetting, adhesive bond formation) can be achieved (Figure 1a). Disulfide bonds have been particularly popular in accessing multifunctional HMAs on account of the bonds’ ability to become dynamic to heat or UV light.1,19,20,32−34 For example, both Michal et al.23 and Cudjoe et al.24 demonstrated the adhesive capabilities of dynamic covalent networks containing disulfide bonds. By disengaging the disulfide bonds using heat (>150 °C) or UV light, the modulus of the material lessened, allowing an adhesive bond to be formed between two glass or metallic substrates. Moreover, this adhesion was reversible, given the dynamic nature of the disulfide bond, and the bond could be reformer repeatedly even after failure. However, the stimuli used to reconfigure these systems (heat and UV light) limited the bonding substrate to either optically clear, UV inert materials or substrates that were capable of withstanding high temperatures (ca. 150 °C). These specifications effectively eliminate the disulfide dynamic networks as applicable adhesives for many common thermoplastics and room-temperature applications. To address these shortcomings, this work seeks to expand the utility of dynamic covalent adhesives through the use of dynamic bonds that undergo exchange at room temperature, with a particular focus on creating materials suitable for PSA applications.

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In order to effectively access room-temperature applications using dynamic network adhesives, the targeted equilibrium reaction should demonstrate reversible behavior in ambient conditions. Recent work by Bowman and co-workers has shown that (catalyzed) room-temperature thiol−thioester exchange can promote pressure-sensitive adhesion in thiol−ene adhesives, with further enhancement through pairing with hard filler particles.1 A series of cross-linkers were prepared with different −R groups, namely, the electron-donating −methoxy (1M), the electronically neutral −hydrogen (1H), and the electron-withdrawing −nitro (1N); see the Experimental Section for synthetic details. Using PMMS and 1X, a series of dynamic polymer networks (2N100, 2N50H50, and 2N50M50, where the subscript denotes the mole percent (mol %) of the BCA crosslinkers (1X) relative to the total amount of thiol) were targeted (Figure 2a). In particular, these systems were chosen to probe the effects of varying equilibrium bonding position and DRIPS morphology on adhesive performance. Of particular interest is the comparison between 2N50H50 and 2N50M50 as it has been previously demonstrated that mixtures of 1N and 1H have an increased degree of phase separation in comparison to equivalent mixtures of 1N and 1M.38 Additionally, the incorporation of more electron-donating cross-linkers (1H and 1M) with strongly withdrawing cross-linkers (1N) effectively lowers the glass transition temperature ($T_g$) and plateau modulus as compared to a parent film composed completely of the stronger acceptor, yielding materials more suitable for pressure-sensitive adhesion (Figure S1).38 To obtain a baseline understanding of the equilibrium bonding behavior of the dynamic polymers, the equilibrium

![Figure 1.](image1.png)

**Figure 1.** (a) Schematic illustration of dynamic covalent networks as adhesive materials. (b) Chemical scheme of generalized BCA-based tM reaction.

![Figure 2.](image2.png)

**Figure 2.** (a) Chemical structures of ditopic electrophiles (1) and PMMS. (b) Illustration demonstrating network (2) formation resulting from the combination of PMMS and 1.
position of mixtures of small-molecule analogues (mono-N, mono-H, and mono-M for \(-\)nitro, \(-\)hydrogen, and \(-\)methoxy, respectively) with 1-octanethiol was carried out over a range of temperatures; see Figure 3a (Figures S2–S4). To simulate the materials, mono-N or equal mixtures of mono-N with either mono-H or mono-M were mixed with an equimolar concentration of thiol (200 mM concentrations of thiol, \(\sim 10\%\) of the concentration of the bulk films). As expected, the equilibrium position of the mono-N solution was higher than that of the either mixed system, with the mono-N/mono-H mixture showing a higher degree of equilibrium bonding than the mono-N/mono-M mixture for all temperatures (Figure 3b). It should be noted that despite this difference, the overall equilibrium position of both the mixed systems was quite similar (71 vs 64% at room temperature), largely a consequence of the competitive bonding between acceptors; see Figure S4 and Table S1. Interestingly, in both hybrid mixtures, the mono-N and mono-H/M acceptors displayed similar decreases in the equilibrium bonding position with increasing temperature as opposed to a preferential debonding of the “weaker” acceptor. This implies that changes in bonding upon heating should occur homogenously throughout the material, outside of phase-separated regions. The temperature-dependent equilibrium behavior also suggests that the overall network connectivity and the resulting adhesive properties will vary depending on the operating temperature.

The similarity in the measured equilibrium position of the model studies would suggest that the mechanical properties of 2N\(_{50}\)H\(_{50}\) and 2N\(_{50}\)M\(_{50}\) may be similar (assuming exchange kinetics occur over similar timescales). To investigate this, the viscoelastic properties of the dynamic networks were probed using small-amplitude oscillatory shear (SAOS) rheometry.

Similar to previous findings, temperature ramp experiments (Figure 4a) revealed two thermal transitions in all dynamic networks. The first thermomechanical \(T_g\) (as defined by the tan \(\delta\) peak) occurred below room temperature for both 2N\(_{50}\)H\(_{50}\) and 2N\(_{50}\)M\(_{50}\) at 15 and 16 °C, respectively, and above room temperature (\(\sim 40\) °C) for 2N\(_{100}\). Notably, the two hybrid samples exhibited a rubbery plateau modulus ranging from 2.8 \times 10^5 to 5.8 \times 10^5 Pa over a temperature range of more than 100 °C (ca. 40–140 °C), implying a large window of operation before the films begin to flow more readily. Importantly, above \(\sim 140\) °C, the two hybrid networks undergo a significant drop in modulus, thereby creating an opportunity for hot melt adhesion. 2N\(_{100}\) also exhibits a drop in modulus at around this temperature, but the drop is less significant. Characteristic of bond dissociation in dynamic networks, the changes to moduli for all systems are accompanied by an increase in the loss modulus (Figure S5) before the samples begin to readily flow. Further thermal characterization of the films via differential scanning calorimetry (DSC) showed the presence of a second higher thermal transition (\(>150\) °C).
To investigate the DRIPS morphology of the dynamic networks, atomic force microscopy (AFM) was carried out (at 0 °C for 2N50H50/2N50M50 and 35 °C for 2N100), and the phase images are shown in Figure 5 (see Figures S6–S8 for height images). In line with prior work on related systems, the 2N50H50 (Figure 5a) sample showed significantly higher degrees of phase separation in comparison to 2N50M50 (Figure 5b), though neither hybrid network displayed the large hard-phase domains found throughout 2N100 (Figure 5c). Interestingly, in the hybrid systems, the small hard-phase regions were largely disconnected, which potentially explains why the SAOS rheology was similar between 2N50H50 and 2N50M50, despite the difference in the hard-phase content. Taken together, the 2N50H50 and 2N50M50 networks have very similar continuous phases while differing starkly in the amount and distribution of hard phase throughout the material, representing an ideal system to assess the impact of DRIPS morphology on adhesive properties.

As an initial investigation into the adhesive properties of the DRIPS networks, SAOS frequency studies were used to further probe the PSA characteristics of the dynamic systems (Figure S9). Frequency sweeps from 0.01 to 100 rad/s were conducted at different temperatures centered around the target operating temperature of 25 °C. Using the time-temperature superposition principle (Figure S10), a master curve was generated at a reference temperature of 25 °C. Figure 6a shows the master curves for 2N50H50 and 2N50M50 as determined by multiple frequency sweeps shifted according to the WLF fit (2N100 was determined to be too glassy at room temperature, Figure S11). Using these master curves, two principles were applied to define their ability to act as PSAs: the Dahlquist criterion and the viscoelastic window (VW). According to the Dahlquist criterion, for materials to be useful as PSAs, they should possess a storage modulus (G′) at 0.01 and 100 rad/s. In a plot of storage vs loss modulus, the values can be used as coordinates to form four corners of a rectangle which constitutes the VW: (1) G′ at 100 rad/s and G″ at 0.01 rad/s, (2) G′ at 100 rad/s and G″ at 100 rad/s, (3) G′ at 0.01 rad/s and G″ at 100 rad/s, and (4) G′ at 0.01 rad/s and G″ at 0.01 rad/s. Their investigation determined that this window varies depending on the PSA application, and as a result, they were able to identify five viscoelastic regimes for PSAs based on the location of their VW in the G′/G″ plot: non-PSA (quadrant 1), high shear PSA (quadrant 2), removable PSA (quadrant 3), cold-temperature PSA (quadrant 4), and general PSA (central region). Using the frequency data acquired for the master curves, it was possible to establish VWs for 2N50H50 and 2N50M50. As shown in Figure 6b, much of the VW for 2N50H50 and 2N50M50 falls in quadrant 2, suggesting that the two materials would perform as high-shear PSAs. These types of PSAs are typically characterized by a high storage modulus which contributes to the higher shear strength relative to other PSAs. Generally, the differences in the VW for 2N50H50 and 2N50M50 highlight the ability to tune the adhesive response through manipulating the electronic nature of the dynamic bond, suggesting that future optimization of the dynamic network composition could target specific PSA applications. To assess the shear resistance of these adhesives, shear adhesion failure temperature (SAFT) tests with a 100 g hanging load were carried out. The SAFT measurements indicated failure temperatures of ∼49 and ∼54 °C for 2N50H50 and 2N50M50, respectively (Figure S12). The trend in the failure temperatures is consistent with the VW predictions, and the relatively low values are likely a consequence of accelerated dynamic exchange inducing creep in the adhesive.

 Inspired by the potential adhesive characteristics of the tM films, the mechanical performance of these materials was assessed for both pressure-sensitive and hot melt adhesion. Three different testing methods were employed to evaluate the adhesive properties of the films: tack and 180-degree peel tests for probing their PSA abilities and normal force pull-off tests to determine their adhesive strength as HMA. To assess the films as PSAs, the hybrid networks were prepared as tapes with Kapton backing on either side (see Experimental Section). To apply, the desired shape was cut from the tape, and the two Kapton sheets were pulled apart to expose the adhesive.
material. This process served to protect the adhesive surface from contaminants and oxidation while also ensuring that the material was firmly attached to the Kapton substrate, facilitating an accurate measurement of PSA properties.

To begin assessing the PSA properties of the tM tapes, tack experiments were carried out. Samples were mounted onto the lower plate of a rheometer, and the top plate was pressed into the adhesive with a varied axial force (0.1, 1.0, and 10 N) for 10 s at room temperature. The force curve was then evaluated for both pull-off strength (peak force reached during the tack test) and adhesive/cohesive strength of tack (area under the force curve). As expected, higher applied force resulted in an increase in both the peak force and the adhesive tack strength (Figure 7a,b). Interestingly, both adhesives demonstrate similar peak forces across the range of applied forces. However, $2N_{50}M_{50}$ did demonstrate enhanced overall tack strength relative to $2N_{50}H_{50}$ with increasing applied force (Figure 7b).

Figure 6. (a) Master curves from the WLF temperature shift factor ($\alpha(T)$) of SAOS rheology frequency studies for $2N_{50}H_{50}$ (violet) and $2N_{50}M_{50}$ (cyan) [amplitude (strain) = 1.0%; reference temperature = 25 °C]. Dashed lines highlight the Dahlquist criterion ($3 \times 10^5$ Pa at 1 rad/s). (b) VWs for $2N_{50}H_{50}$ (violet) and $2N_{50}M_{50}$ (cyan) with corner numbers (1–4) corresponding to modulus values from master curves in plot a. Gray region highlights moduli outside of the typical VW plot.

Figure 7. Graphical summary of the (a) peak force and (b) adhesive strength for tack test of $2N_{50}H_{50}$ (violet) and $2N_{50}M_{50}$ (cyan) with the variable applied force (8 mm parallel plate, 10 s application time, and 0.1 mm/s strain rate). (c) Graphical representation of the peak force for 10 consecutive repeat tack experiments on $2N_{50}H_{50}$ (squares) and $2N_{50}M_{50}$ (circles) (8 mm parallel plates, 0.1 mm/s strain rate, 60 s adhesion time, and 1.0 N applied force).
This result is potentially a consequence of the resistance to flow of the larger amount of hard phase in 2N50H50. As such, the tack strength of 2N50H50 could be increased by extending contact times, presumably giving the hard-phase domains time to redistribute themselves (Figure S13). Interestingly, 2N100 (which was not suited for room-temperature PSA applications) did not yield measurable PSA performance even at elevated temperatures (up to 120 °C, Figure S14), presumably a result of a higher overall amount of large hard-phase domains relative to the mixed systems.

A critical parameter of PSAs is their ability to maintain their adhesive properties over several cycles. Generally speaking, a PSA functions under working conditions that are relatively short in adhesion time and small in applied force over the course of several bonding cycles. As such, the performance of the dynamic adhesives under cyclic loading conditions was assessed using a middling set of parameters (60 s adhesion time and 1 N applied force). Using the same tack test setup as previously described, samples of each material were tested for 10 consecutive tack cycles at room temperature (Figure 7c). Comparing the tack of the two materials, 2N50H50 shows a stark drop in the peak force after the first bonding cycle, possibly arising from difficulties in rearranging the hard-phase domains after the initial loading conformation. Despite this drop in performance, it is important to note that both hybrid materials had overlapping values of peak tack force (~4.5 N) and tack strength (~15 Ns) for all cycles, excluding the first (Figure S15). These results highlight that both DRIPS adhesives displayed relatively consistent PSA characteristics over the course of repeated adhesions, demonstrating the rebondability of these materials.

Another useful metric for assessing the PSA performance is the peel strength. To investigate the peel performance of the DRIPS adhesives, the tapes were evaluated using a 180-degree peel test at room temperature. Prior to testing, the tapes were peeled at a 180° angle onto the exposed adhesive surface. The foil strip was then bonded assembly. To evaluate their performance as HMAs, squares of the original pressed DRIPS films (not tape) were used to adhere two aluminum I-bars together at 180 °C. Once cooled, the two I-bars were loaded into a uniaxial tensile testing apparatus, and the adhesive strength of the film was determined (Figure 9a). The strongly bound 2N100 material, while unable to perform as a PSA due to the high glass transition temperature, performed impressively in a hot melt context, leading to high values of adhesive strength (0.80 ± 0.07 MPa). In agreement with the temperature ramp rheology studies, the 2N100 material did not undergo a significant amount of flow even when processed at 180 °C (Figure 9b). However, despite the glassy nature of 2N100, the samples failed cohesively, implying strong adhesion to the aluminum substrate.

Despite their ability to deform at room temperature, both 2N50H50 and 2N50M50 demonstrated impressive adhesive strengths when applied as HMAs, particularly 2N50H50 whose performance (0.81 ± 0.1 MPa) matched that of 2N100. In the case of both hybrid materials, the initial ~5 × 5 × 0.4 mm material underwent significant flow when processed at 180 °C, leaving much larger cohesive failure footprints (Figure 9c,d) than those left by 2N100, thereby acting as more efficient HMAs on a volumetric basis (force values in Figures 9a and S17b). The outstanding HMA performance of 2N50H50 is largely a result of the relatively high amount of hard-phase domains throughout the sample, which efficiently dissolve/spread upon exposure to high temperatures and act to bridge substrates upon cooling. This result clearly demonstrates the potential impact of tuning the morphology of DRIPS-based adhesives, which enables the targeting of performance parameters ranging from low strength, rebondable PSAs to high-strength HMAs.

**CONCLUSIONS**

Hybrid TM networks composed of ditopic acceptor compounds (1) and an oligomeric thiol component (PMMS) demonstrated the ability to function as both PSAs and HMAs. Their viscoelastic behavior at room temperature met the Dahlquist criterion (modulus < 3 × 10^7 Pa at a testing frequency of 1.0 rad/s), indicating their potential for use as PSAs. Cyclic tack
The filtrate was washed thoroughly (three or more times) with brine (sodium chloride-saturated water) and dried with magnesium sulfate. DCM was removed from the solution via rotary evaporation, and the resulting yellow oil was dried overnight under high vacuum (MW = 284.15 g/mol, yield = 70% by mass). 1H NMR [500 MHz in CDCl3; δ ppm: 3.54 (s, 2H), 3.68 (s, 2H), 3.76 (t, 2H), and 4.39 (t, 2H)].

13C NMR (101 MHz in CDCl3; δ 163.11, 112.99, 70.68, 68.62, 65.77, 24.73).

**TEG Bis(4-nitrobenzalcyanoacrylate) (1N)**. TEG bis-(cyanoacrylate) (1, 5 g, 0.018 mol, 0.14 M) and 4-nitrobenzaldehyde (5.74 g, 0.038 mol) were added to a 250 mL round-bottom flask with DCM (130 mL) and 0.15 M equivalents of catalytic triethylamine (TEA, 0.3 mL, 0.003 mol). The flask was then placed under a nitrogen atmosphere and allowed to stir using a magnetic stir bar overnight. DCM was removed using rotary evaporation, and the resultant oil was triturated in MeOH for 2 h. The solution was filtered, and a solid powder was collected. This trituration process was repeated until the filtrate was clear and colorless, leaving behind a reddish, claypy powder. 1H NMR [500 MHz in CDCl3; δ ppm: 3.77 (s, 2H), 3.89 (s, 2H), 4.54 (t, 2H), 8.16 (d, 2H), 8.34 (s, 1H), and 8.37 (d, 2H)].

13C NMR (126 MHz in CDCl3; δ 161.95, 152.06, 149.78, 136.82, 131.59, 124.36, 114.36, 106.90, 70.68, 68.62, 65.77). Yield by mass = 45%.

**TEG Bis(benzalcyanoacrylate) (1H)**. TEG bis(cyanoacrylate) (1, 5.00 g, 0.018 mol, 0.14 M) and benzaldehyde (4.03 g, 0.038 mol) were added to a 250 mL round-bottom flask with DCM (130 mL) and 0.3 M equivalents of catalytic TEA (0.3 mL, 0.003 mol). The flask was then placed under a nitrogen atmosphere and allowed to stir using a magnetic stir bar overnight. DCM was removed using rotary evaporation, and the resultant oil was triturated in MeOH for 2 h. The solution was filtered, and a solid powder was collected. This trituration process was repeated until the filtrate was clear and colorless. 1H NMR [500 MHz in CDCl3; δ ppm: 3.77 (s, 2H), 3.88 (t, 2H), 4.51 (t, 2H), 7.53 (t, 2H), 7.58 (t, 1H), 8.01 (d, 2H) and 8.28 (s, 1H)].

13C NMR (101 MHz in CDCl3; δ 162.51, 155.35, 133.40, 131.45, 131.15, 129.30, 115.36, 102.80, 70.90, 68.80, 65.81). Yield by mass = 51%.

**TEG Bis(4-methoxybenzalcyanoacrylate) (1M)**. TEG bis-(cyanoacrylate) (1, 5.00 g, 0.018 mol, 0.14 M) and 4-methoxybenzaldehyde (5.17 g, 0.038 mol) were added to a 250 mL round-bottom flask with DCM (130 mL) and 0.15 M equivalents of catalytic TEA (0.3 mL, 0.003 mol). The flask was then placed under a nitrogen atmosphere and allowed to stir using a magnetic stir bar overnight. DCM was removed using rotary evaporation, and the resultant oil was triturated in MeOH for 2 h. The solution was filtered, and a solid powder was collected. This trituration process was repeated until the filtrate was clear and colorless. 1H NMR [500 MHz in CDCl3; δ ppm: 3.77 (s, 2H), 3.87 (t, 2H), 3.91 (s, 3H), 4.48 (t, 2H), 7.01 (d, 2H), 8.02 (d, 2H), and 8.20 (s, 1H)].

13C NMR (101 MHz in CDCl3; δ 163.86, 163.14, 154.66, 133.74, 124.36, 116.08, 114.79, 109.14, 70.90, 68.87, 65.54, 55.64). Yield by mass = 51%.

**Synthesis of tM Networks (2)**. tM networks were prepared following previously reported methods with minor modifications. Briefly, ditopic Michael acceptors (1, Figure 1c) and PMMS (Figure 1c) were dissolved in chloroform, stirred for 2 h at 50 °C, and cast onto Teflon drying dishes. The films were dried overnight at room temperature and then transferred to a vacuum oven at 60 °C and dried under reduced pressure for 24 h. The networks were then heated to 150 °C and held isothermally under a reduced pressure for 30 min to remove any trapped solvent before compression molding. The sample films were pressed at 70 °C for 10 min under 10 kpsi (films containing only PMMS were pressed at 90–120 °C). In total, three tM networks were prepared: 2N50H50 as well as two hybrid materials composed of 1N with 1H (2N50H50) and 1N with 1M (2N50M50). The subscript denotes the mole percent (mol %) of each acceptor (a = 100 or 50) relative to the total amount of thiol.

**Thermogravimetric Analysis**. Thermogravimetric analysis was performed using a TA Instruments Discovery thermogravimetric analyzer in the Soft Matter Characterization Facility at the University of Chicago. Samples were tested under a nitrogen atmosphere using
platinum pans. Tests were conducted using a ramp of 10 °C/min from the starting operation temperature (ca. 35 °C) to 600 °C.

Nuclear Magnetic Resonance. Nuclear magnetic resonance (NMR) was performed using a 500 MHz Bruker AVANCE II+ 500 11.7 T NMR or a Bruker AVANCE III HD 500 11.7 T NMR spectrometer at the NMR facilities at the University of Chicago. For experimental temperatures in the range of 25–45 °C, a standard plastic sample spinner was used; for equilibrium measurements at or above 55 °C, a ceramic spinner was used. Sample temperatures were measured through the use of an ethylene glycol standard; see the Supporting Information for further information.

DSC. DSC was performed using a TA Instruments Discovery 2500 differential scanning calorimeter in the Soft Matter Characterization Facility at the University of Chicago. Samples were prepared in aluminum hermetic pans from TA Instruments and were hermetically sealed. Typical test conditions involved a cool–heat–cool–heat procedure from (−20 °C/200 °C/−80 °C/200 °C) with a rate of 10 °C/min.

Rheology. Rheology was performed using a TA Instruments RSA-G2 ARES rheometer with a forced convection oven (20–500 °C) attached to an air chiller system (−120–20 °C) and running TA Trios software in the Soft Matter Characterization Facility at the University of Chicago. An 8 mm stainless steel parallel plate was used for all tests. For frequency sweeps, the sample was equilibrated at the testing temperature for 5 min before the experiment was started. After equilibration, a frequency sweep from 0.01 to 100.0 rad/s was done at 1.0% strain. Subsequent sweeps were conducted by increasing the temperature by 5 °C and re-equilibrating for 5 min before beginning the frequency experiment.

Tensile Analysis. Tensile analysis was performed using a Zwick-Roell zwickLine Z0.5 materials testing instrument with either a 100 N (peel tests) or 500 N (hot melt tests) load cell in the Soft Matter Characterization Facility at the University of Chicago.

AFM. AFM images were collected using an Asylum Research Cypher ES Environmental microscope. Tapping-mode imaging was performed using Asylum Research FS-1500-AuD cantilevers with resonant frequencies of 1.5 MHz. Images were collected at a scan rate of 2 Hz (for 2N<sub>100</sub> or 5 Hz (for 2N<sub>50M50</sub> and 2N<sub>50H50</sub>) with a 500 mV set point in the repulsive mode (to prevent tip-induced damage of the sample surface). To achieve adequate phase contrast/image clarity, samples were imaged at 35 °C (for 2N<sub>100</sub>) or 0 °C (for 2N<sub>50M50</sub> and 2N<sub>50H50</sub>) in an argon atmosphere with cell gauge pressures of 30 mbarg. Samples were equilibrated for 5 min at the desired temperature prior to imaging. Images were processed with a first-order flatten.

Preparation of TM Adhesive Tapes. The film of interest was pressed between two Kapton sheets at 200 °C and 1 kpsi for 10 min, creating an adhesive layer that was approximately 100 μm thick. Tapes were cooled to room temperature on the benchtop and stored at −20 °C until needed.

Tack Tests. The tack of the TM tapes was evaluated using a TA Instruments ARES-G2 rheometer equipped with an 8 mm stainless steel parallel plate. Samples were cut in 8 mm × 8 mm squares and mounted onto the lower plate using double-sided tape. An axial force (0.1 N, 1.0 N, or 10 N) was applied to the sample for a predetermined period of time (20 s, 60 s, or 120 s) after which the upper plate was removed from the adhesive at a constant rate of 0.1 mm/s.

180° Peel Tests. The adhesive tape was cut into a strip ca. 5 mm wide and 70 mm long. The strip was adhered to a glass microscope slide using a strong cyanoacrylate-based adhesive. The free Kapton surface was removed immediately prior to testing, and a strip of aluminum foil (approximately 10 mm wide and 200 mm long) was adhered to the TM adhesive by rolling with a weighted 1 kg roller (taking care to not exert additional force onto the sample). The aluminum foil was folded in half, and the setup was mounted onto the Zwick grips. Peel tests were run for a travel distance of 50 mm at a strain rate of 10 mm/min.

Hot Melt Adhesion Tests. A 5 mm × 5 mm square of the original pressed films (not tape) was situated between two aluminum I-bars which were then clamped together with clips. The entire setup was placed in an oven at 180 °C for 10 min after which it was removed and allowed to cool on the benchtop with the clips attached for another 10 min. Once cooled, the clips were removed, and the adhered I-bars were loaded onto the Zwick clamps. Adhesive strength of the hot melt bond was measured at 1 mm/min, and the area used for calculating the adhesive strength was estimated from the average area of the circular adhesive footprint left after the bond failed.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c05813. Additional characterization of adhesive networks including TGA, DSC, temperature-dependent NMR methods, and spectra, AFM height traces, SAOS frequency sweeps, and adhesive test results (PDF)

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Notes

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