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Unraveling the Properties of Ultrahigh Molecular Weight Polyacrylates

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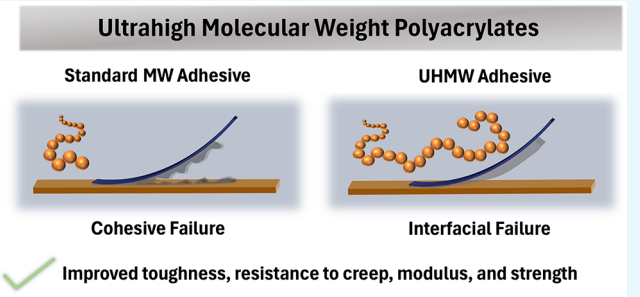
ABSTRACT: Photoiniferter polymerization is a straightforward method to produce well-defined ultrahigh molecular weight (UHMW, >1 MDa) acrylate polymers, which potentially provides access to a generation of advanced materials. However, the role of UHMWs on the properties of these materials is not thoroughly understood. Herein, we show that the molecular weight of UHMW poly(methyl acrylate) (PMA) has a significant impact on its mechanical properties. We observed that the mechanical and thermal properties of PMA are dramatically improved at UHMW. Based on these findings, we successfully heightened the cohesive strength and thermal stability of pressure-sensitive adhesives without the need for cross-linkers, which are traditionally required in adhesive materials. These findings highlight the potential of UHMW polyacrylates in the development of robust materials.



KEYWORDS: *Polyacrylate, poly(methyl acrylate), ultrahigh molecular weight, pressure-sensitive adhesives, photoiniferter polymerization*

Since its invention in 1953 by chemists at the Max Plank Institute, ultrahigh molecular weight polyethylene (UHMWPE) has revolutionized the polymer industry and is expected to reach a market size of $3.3 billion by 2027.[1,2] UHMWPE can be synthesized with molecular weights up to 7.5×10^6 Da to produce a plastic with exceptional properties, such as high abrasion and fracture resistance and tensile strength approximately eight times greater than that of high-strength-grade steel by weight.[1,3] These distinctive characteristics have made UHMWPE suitable as a component of hip implants, body armor, truck beds, and marine gear.[1,4]

Given the unprecedented qualities of UHMWPE, the development of synthetic methods to produce other UHMW polymers (UHMW, $>10^6$ Da) has been an area of increased attention. When seeking to elucidate the role of molecular weight on polymer properties, it would be beneficial to prepare polymers that are not only UHMW but also well-defined in terms of their dispersity and architecture. Controlled polymerization techniques allow for the synthesis of well-defined UHMW polymers, with success having been demonstrated via cationic ring-opening polymerization, atom transfer radical polymerization, and reversible addition−fragmentation chain-transfer polymerization.[5−7] The latter two methods are examples of reversible-deactivation radical polymerization (RDRP), where UHMWs can be targeted by employing conditions that maximize the rate of propagation relative to termination.

Photomediated RDRP offers the benefits of spatiotemporal control and straightforward reaction conditions.[6,8−14] These advantages enable applications such as additive manufacturing and have been shown to eliminate the need for conditions such as high pressures or heterogeneous methods often required to reach UHMWs in other systems.[7,15,16] Photoiniferter polymerization is an example of a light-mediated RDRP method that uses a molecule capable of photolysis (*iniferter*) that can engage in *ini*tiation of polymer chains, degenerative chain trans*fer*, and reversible *ter*mination.[8,17,18] Photoiniferter polymerization has been successfully applied to achieve a variety of UHMW polymers (>5 MDa) with predictable molecular weights and dispersities as low as $Đ = 1.1$.[19]

Polymer mechanical properties correlate with molecular weight and have been studied for UHMW polymers prepared by recently developed synthetic methods.[5,20] UHMW polydioxolane (M_n > 2 MDa) synthesized by cationic ring-opening polymerization was tough and ductile with ultimate tensile strength exceeding that of UHMWPE.[5] The mechanical properties of methacrylate-based UHMW polymer gels synthesized in ionic liquids have also been investigated.[20] Physical cross-links from chain entanglements maintained the integrity of the gels, and the networks exhibited increases in ultimate tensile strength and resistance to creep at higher molecular weight.[20] Despite these examples, little research on

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the mechanical properties of UHMW acrylate-based polymers has been performed.

Two types of interchain interactions are involved in thermoplastic polymer systems and contribute to their observed physical properties, namely, intermolecular forces and topological entanglements.[21,22] Below the glass transition temperature (T_g) and at low strains, intermolecular forces are more prevalent than topological entanglements and, therefore, contribute to polymer properties to a greater extent by restricting long-range cooperative backbone mobility. As temperature rises above the T_g or strains increase, topological entanglements or cross-links become increasingly important in dictating material properties by behaving as physical cross-links that cause an increase in viscosity and thermal stability and improve mechanical properties such as shear resistance, important characteristics of pressure sensitive adhesives (PSAs).[23−25]

PSAs are capable of binding to a variety of surfaces upon application of mild pressures over short time scales and typically have a T_g below room temperature.[25] Various types of PSAs exist, including silicones, polyurethanes, epoxies, and acrylics.[25] Acrylic PSAs, in particular, have recently dominated the PSA market due to their high tack, transparency, and resistance to UV light, oxidation, heat, and humidity.[25] Designing functional PSAs requires a careful balance of tack/adhesion and cohesion.[26] Since cohesive failure leaves residue on the substrate, an ideal PSA would show exceptional adhesion and tack and fail interfacially. Because entanglements in commercial adhesives are insufficient in preventing cohesive failure and creep, PSAs are often cross-linked, improving cohesive strength, albeit at the expense of adhesion.[25] We hypothesized that increasing the molecular weight of acrylate-based polymers to UHMWs would accentuate the effects of chain entanglements to enhance cohesive strength and eliminate the need for cross-linkers in acrylate PSAs.

Herein, we report the effect of molecular weight and temperature dependency on the mechanical properties of UHMW poly(methyl acrylate) (PMA) synthesized via photoiniferter polymerization. We sought to understand the influence of increased chain entanglements within the UHMW regime on the material properties that are dominated by intermolecular interactions below the T_g and topological entanglements above the T_g (Figure 1). Furthermore, we hypothesized that by leveraging the increased effect of chain entanglement within the rubbery plateau region of UHMW acrylates, the cohesive performance of PSAs could be enhanced without the addition of a cross-linker. This work provides fundamental insight into the emerging field of controlled UHMW polymers by exploring the role of chain length on polyacrylate PSA performance.

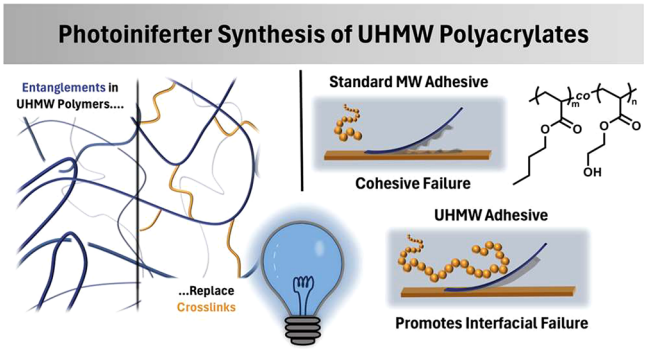

Figure 1. Depiction of the advantages of UHMW polyacrylates synthesized via photoiniferter polymerization. (Left) Entanglements serve as physical cross-links, mimicking the role of chemical cross-links in conventional pressure-sensitive adhesives and improving mechanical and thermal network stability. (Right) Adhesive chemical structure and failure mechanism as a function of molecular weight.

RESULTS AND DISCUSSION

PMAs with molecular weights (M_n) of 0.2, 1, and 2 MDa were synthesized using photoiniferter polymerization to study the effect of molecular weight within the UHMW regime on the mechanical properties of polyacrylates (Figure S1). After purification, we successfully obtained each targeted product (number-average molecular weight (M_n): 0.25, 1.0, and 2.1 MDa as determined by size-exclusion chromatography (SEC) and ^{1}H NMR spectroscopy (Figure 2A, Figures S2−S4)).

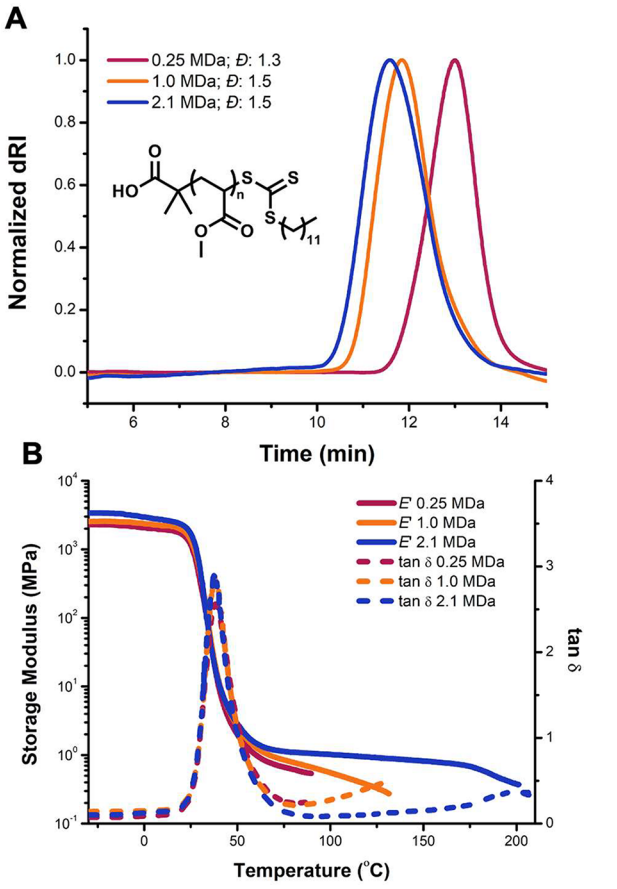

Figure 2. (A) Size exclusion chromatography (SEC) and (B) dynamic mechanical analysis (DMA) temperature ramps showing the modulus and tan δ until material failure in the terminal region for poly(methyl acrylate) (PMA) with M_n = 0.25, 1.0, and 2.1 MDa.

The thermal properties of the three PMA polymers were measured using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Figures S5−S6). The minimal weight loss observed in each case up to 300 °C was likely from loss of the photoiniferter end-group,[27] and no appreciable difference between samples of varying M_n was observed for T_{95} (Tables S1−S2). The T_g was determined by DSC (Figure S6) and was essentially the same between the samples (~17−18 °C), in agreement with the Flory−Fox

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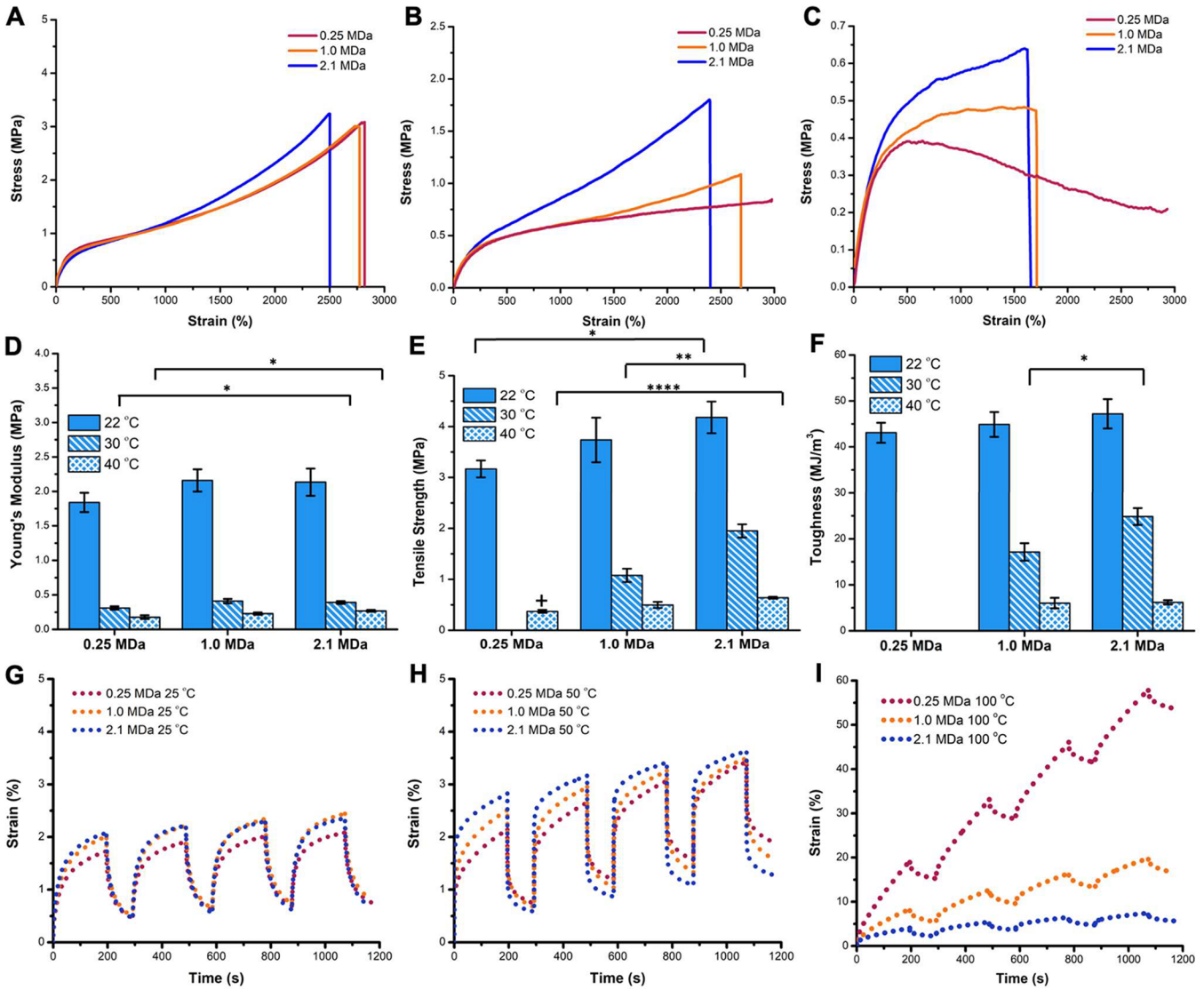

Figure 3. Representative stress−strain curves for poly(methyl acrylate) (PMA) of 0.25, 1.0, and 2.1 MDa at (A) 22 °C, (B) 30 °C, and (C) 40 °C. The (D) Young's modulus, (E) tensile strength, and (F) toughness were extracted from the tensile stress−strain curves of PMA. * $p \leq 0.05$; ** $p \leq 0.01$; **** $p \leq 0.0001$; + tensile strength at yield. Creep cycles were measured under 500 Pa of stress for PMA of 0.25, 1.0, and 2.1 MDa measured at (G) 25 °C, (H) 50 °C, and (I) 100 °C.

prediction.[28] Prior to mechanical testing, PMAs of 0.25 and 1.0 MDa were compression molded at 125 °C for 2.5 h. Because of the exponential increase in viscosity with molecular weight, the PMA of 2.1 MDa could not be molded under these conditions. To allow flow under compression in a time-efficient manner and to avoid damage caused by long-term heat exposure, the PMA of 2.1 MDa was compression molded at 150 °C for 2.5 h.

To further probe the role of chain entanglement as a function of molecular weight in the rubbery plateau region, each sample was subjected to dynamic mechanical analysis (DMA) under a 0.05% oscillatory strain (Figure 2B, Tables S3−S4). An increase in the height and breadth of the rubbery plateau region was observed with an increase in molecular weight, suggesting an enhancement in the effect of chain entanglements with molecular weight.

While the effect of chain entanglements was expected to be most pronounced above the T_g (~37 °C from DMA), we sought to also understand the effect of molecular weight on the mechanical behavior as the polymer softened through the T_g. Consequently, each sample was subjected to tensile testing at a strain rate of 0.5 mm/s at 22, 30, and 40 °C. All samples displayed elastomeric behavior under each condition (Figure 3A−C). As the temperature increased, a change in material behavior was observed. The PMA of 2.1 MDa showed strain hardening before failure at all temperatures. In contrast, PMA of 1.0 MDa strain hardened at lower temperatures, but at 40 °C, this behavior was no longer observed. Finally, substantial yielding occurred for the PMA of 0.25 MDa when tested at 40 °C. We attribute these differences in elastomeric behavior to the increased effect of chain entanglements with increasing molecular weight.

Young's modulus, ultimate tensile strength, strain at break (%), and toughness were extracted from the stress−strain curves for a minimum of five samples of each polymer (Figure 3D−F, Figure S7, Tables S5−S8). Because of the high-strain capability of PMA of 0.25 MDa, the tensile tester reached limits at 30 and 40 °C before material failure, preventing complete analysis of tensile strength and toughness. (Note: All tensile strength values were extracted from the stress−strain curves at break except for the PMA of 0.25 MDa measured at

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40 °C, where the values were obtained from yield.) A two-sample statistical *t*-test was used to compare samples of differing molecular weights at each temperature to understand the influence of molecular weight on each of the properties. Analysis revealed remarkable enhancement in modulus, tensile strength, and toughness with increasing molecular weight at 30 °C (Table S9) even though the testing temperature was below the reported T_g by DMA (~37 °C), showing the significance of chain entanglements within the glass transition as the polymer softens. An increase in modulus at 40 °C and tensile strength at 22 and 40 °C with molecular weight was also observed. Importantly, the improvement in the tensile strength with molecular weight was more significant at 40 °C where chain entanglements were expected to dominate compared to 22 °C (Table S9). No change in strain at break (%) at any temperature was found with molecular weight. Increasing the molecular weight of PMA to UHMWs improves performance by enhancing the modulus, tensile strength, and toughness. This is crucial as temperatures rise and the effects of chain entanglements become more significant as the PMA softens through the T_g.

Unfortunately, due to a low signal-to-noise ratio, we could not further characterize the tensile properties of the PMA samples at higher temperatures. To probe the effect of molecular weight on the properties of PMA at elevated temperatures, we subjected each sample to creep cycles under 500 Pa of stress at 25, 50, and 100 °C (Figure 3G–I). The results showed no significant effect of molecular weight on the permanent deformation after four creep cycles at 25 °C, further demonstrating that entanglements contribute less significantly to the polymer mechanical properties when temperatures are below the T_g. In contrast, at higher temperatures of 50 and 100 °C above the T_g, decreasing molecular weight led to an increase in permanent deformation. Additionally, at 25 and 50 °C, increasing molecular weight resulted in a higher elastic component, but at 100 °C, the enhanced elasticity observed in the UHMW polymers was no longer present. We attribute the stark difference in permanent deformation and elasticity of the PMA of 0.25 MDa compared to the PMA of UHMW at 100 °C to the loss of network integrity occurring at lower temperatures with decreasing molecular weight as shown by the shift in the onset of the terminal region measured by DMA.

Because we detected minimal effect of molecular weight on the measured properties in the glassy region ≤ 25 °C, we propose that the entanglements play a more significant role in improving the mechanical properties relative to intermolecular forces. The tensile strength was the only property that increased with molecular weight at temperatures ≤ 25 °C. At 30 °C, the toughness and tensile strength were markedly improved with molecular weight, and the material largely retained its elasticity, allowing it to store considerable energy through elastic deformation. At elevated temperatures, the improved elasticity in UHMW samples was lost. Additionally, as molecular weight increased, the onset of the terminal region shifted to significantly higher temperatures, improving the resistance to creep. Overall, these results show that higher molecular weight enhanced modulus, tensile strength, resistance to creep, and toughness even at elevated temperatures and gives insight into the behavior of UHMW acrylates from the glassy to the rubbery states.

Based on the increased effect of chain entanglements on the tensile strength of UHMW PMA, we hypothesized that UHMW polyacrylates would yield PSAs with high cohesive strength without the addition of chemical cross-linkers. To test this hypothesis, three additional acrylate polymers were synthesized using photoiniferter polymerization of butyl acrylate (BA) and 2-hydroxyethyl acrylate (HEA) (5 wt %) as soft and hard monomers, respectively.[29] Throughout the copolymerization, monomer consumption was monitored by ^{1}H NMR spectroscopy, and the linearity of the pseudo-first-order kinetic plot indicated constant radical concentration and steady rate of monomer consumption over time after an inhibition period (Figures S8–S10). Low dispersity, a uniform shift in the SEC traces to shorter elution time, and close correlation of theoretical and experimental molecular weight suggested that the copolymerization was controlled (Figures S11–S16). Analysis of the final molecular weights by SEC demonstrated that the synthesis of UHMW PSAs was successful ([M_n: 0.28 MDa, $Đ$: 1.1], [M_n: 1.3 MDa, $Đ$: 1.3], [M_n: 2.3 MDa, $Đ$: 1.2] (Figure 4)). After purification, ^{1}H

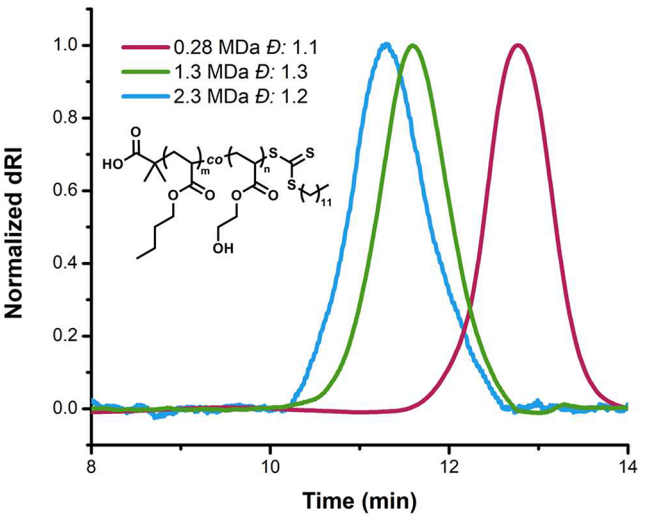

Figure 4. SEC chromatography for the poly(HEA-*co*-BA) adhesives of 0.28, 1.3, and 2.3 MDa.

NMR spectroscopy revealed that the targeted ratio of incorporation of BA/HEA (17.2) was achieved for all adhesives (Figures S17–S19 and Table S10). Thermal analysis with TGA revealed decreasing T_{95} with increasing molecular weight (Figure S20 and Table S11), and DSC showed that the T_g was significantly below room temperature, a crucial characteristic for adhesives to flow onto the substrate during adhesion (Figure S21).

The viscoelastic behavior of the PSAs was evaluated using oscillatory shear rheology (Figure 5A–C). Generally, behavior at high and low frequencies gives information on debonding and bonding, respectively.[26] A higher tan δ in the low-frequency region indicated greater capacity of lower molecular weight adhesives to dissipate energy, thereby allowing flow onto the substrate. In the low-frequency range, lower molecular weights show more dramatic decreases in G', signaling lower resistance to shear with decreasing molecular weight. Since G' remained largely constant within the measured frequency range at 25 °C for the 1.3 and 2.3 MDa adhesives (Figures S22–S23), we expanded the temperature range and horizontally translated the modulus versus angular frequency using time–temperature superposition with a reference temperature of 25 °C. Both UHMW adhesives

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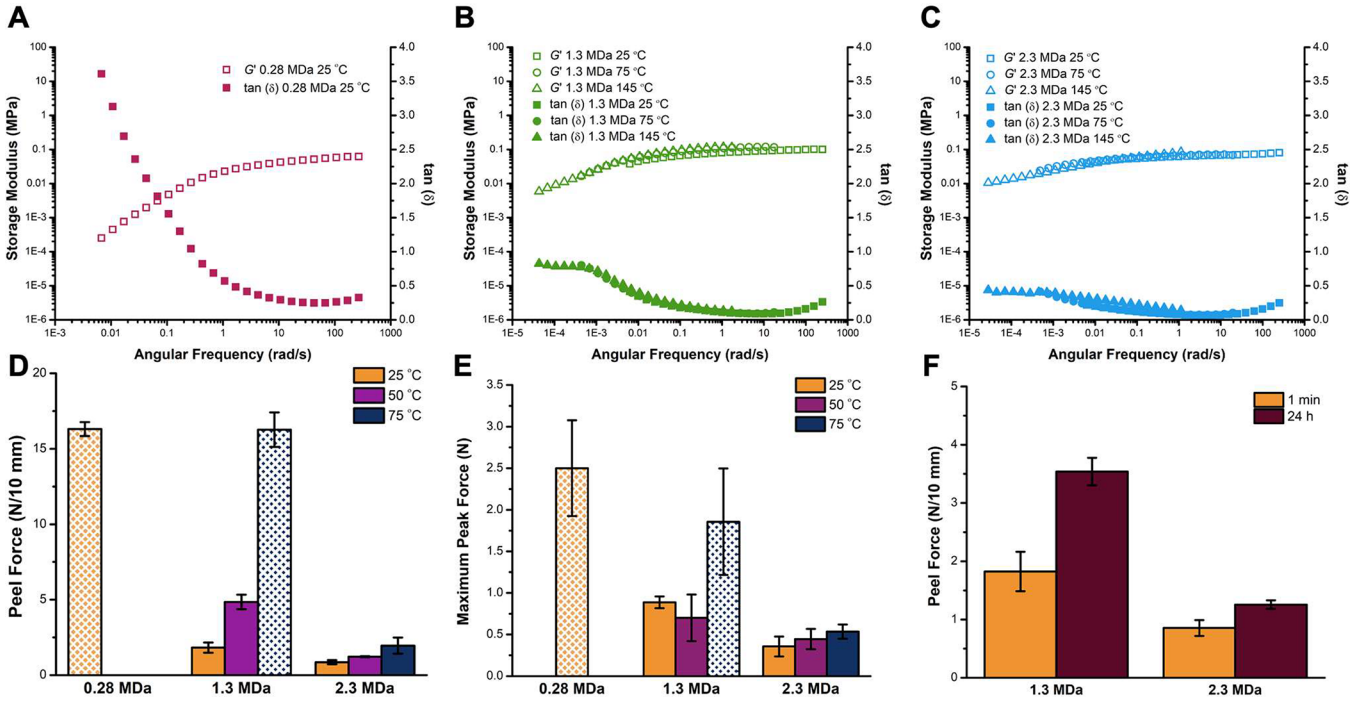

Figure 5. Adhesive testing results for P(BA-*co*-HEA) of 0.28, 1.3, and 2.3 MDa. Time−temperature superposition master curves for P(BA-*co*-HEA) of (A) 0.28 MDa, (B) 1.3 MDa, and (C) 2.3 MDa. (D) Peel force values from 180° peel test as a function of molecular weight and temperature. (E) The maximum peak force measured during loop tack measurements as a function of molecular weight and temperature. (F) Results from 180° peel tests at 25 °C after a residence time of 1 min and 24 h. Peak force values were obtained from the maximum force required to remove the sample from the substrate surface immediately after contact. Peel force values were collected after 1 min of residence time unless otherwise indicated. Dotted bars signify cohesive failure.

showed a significant increase in the tan δ and a decrease in the modulus beyond 0.01 rad/s, indicating that a longer residence time may benefit bonding. All adhesives showed $G' < 10^5$ Pa and satisfied the Dahlquist contact criterion at low frequencies, meaning sufficient surface wetting is possible.[30]

From the results of the frequency sweep, we expected an enhancement in cohesive strength and a reduction in both adhesive strength and tack with increasing molecular weight. The adhesive properties were studied using 180° peel and loop tack tests (ASTM D3330 and ASTM D6195) (Figure S24A). Each of the adhesives was initially tested at room temperature. The adhesive of 0.28 MDa was shown to fail cohesively, but the adhesives of UHMW debonded interfacially (Figure 5D), suggesting that increasing chain entanglements could be effective in improving cohesion (Figure S24B). However, both tack and adhesion decreased with molecular weight, attributed to inhibited chain mobility with molecular weight preventing rapid surface wetting (Figure 5D). To study the effect of temperature on the cohesion, adhesion, and tack of the UHMW (1.3 and 2.3 MDa) adhesives, 180° peel and loop tack experiments were conducted at 50 and 75 °C (Figure 5D−E). Since the 0.28 MDa adhesive showed cohesive failure or network tearing at 25 °C and we sought to understand the effect of temperature on cohesive stability in the UHMW adhesives, we did not further probe the peel and loop-tack behavior at elevated temperatures, which would only serve to promote undesirable cohesive failure more readily. An increase in peel strength was observed for both UHMW adhesives, attributed to the improved diffusion of polymer chains at elevated temperatures (Figure 5D). On the other hand, no differences outside of error were found in the peak force as a function of temperature for both the 1.3 and 2.3 MDa adhesives (Figure 5E). Higher temperatures enabled enhanced flow of the polymer under an applied force, improving the peel force of adhesion with temperature; however, since tack controls how quickly adhesives bond to surfaces with near-zero application force and is a measure of the ability of an adhesive to wet a surface, we propose that the lack of improvement in tack with increasing temperature was caused by the limited capability of the UHMW polymer chains to spontaneously flow without a substantial applied force. Notably, the polymer of 1.3 MDa failed cohesively at 75 °C, leaving residue on the substrate, while the polymer of 2.3 MDa debonded interfacially, showing that by increasing the molecular weight, the thermal stability of the adhesive improves, allowing UHMW adhesives to perform well without the addition of cross-linkers in applications requiring elevated temperatures. To determine if the adhesion could be improved over time, the residence time of the samples was increased from 1 min to 24 h. An increase in the peel strength of the UHMW adhesives by 95% and 48% for the polymers of 1.3 and 2.3 MDa, respectively (Figure 5F), was observed, indicating that long-term residence is effective for UHMW polymers to adhere to surfaces.

CONCLUSION

Using the straightforward synthesis conditions of photoiniferter polymerization, PMA of UHMW was produced, and the mechanical properties were studied as a function of molecular weight and temperature. Compared to their lower molecular weight counterparts, polyacrylates of UHMW exhibited significant enhancements in modulus, tensile strength, creep resistance, and toughness. Moreover, the stabilizing effect of chain entanglements in UHMW poly-

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acrylates significantly improved mechanical stability even at elevated temperatures. These results suggest that UHMW acrylate polymers could find application in cross-linker-free products requiring mechanical and thermal stability, greater strength, toughness, and creep resistance. We utilized the enhanced effect of chain entanglements on the material strength of polyacrylates of UHMW to design PSAs without chemical cross-linkers. As molecular weight increased, the cohesion improved. Furthermore, increasing the molecular weight enhanced the cohesive stability at elevated temperatures, showing the potential effectiveness of UHMW polymers in adhesives for applications at elevated temperatures. These results offer valuable and fundamental insights into the mechanical properties of controlled UHMW acrylate polymers and serve as a foundation for research to discover more beneficial applications of UHMW acrylates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.3c02191.

Materials, instrumentation, synthesis, and supplementary figures (PDF)

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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