Network Polymer Properties Engineered through Polymer Backbone Dispersity and Structure

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Abstract

Dispersity (\mathcal{D} or M_w/M_n) is an important parameter in material design and as such can significantly impact the properties of polymers. Here polymer networks with independent control over the molecular weight and dispersity of the linear chains that form the material are developed. Using a RAFT polymerization approach a library of polymers with dispersity ranging from 1.2-1.9 for backbone chain-length (DP) 100, and 1.4-3.1 for backbone chain-length 200 were developed and transformed to networks through post-polymerization crosslinking to form disulfide linkers. The tensile, swelling, and adhesive properties were explored, finding that both at DP 100 and DP 200 the swelling ratio, tensile strength, and extensibility were superior at intermediate dispersity (1.3-1.5 for DP 100 and 1.6-2.1 for DP 200) compared to materials with either substantially higher or lower dispersity. Furthermore, adhesive properties for materials with chains of intermediate dispersity at DP 200 revealed enhanced performance compared to the very low or high dispersity chains.

Introduction

The molecular structure of a macromolecule is intimately tied to the performance of the polymeric material in a given application.^{1–3} Changes in branching and molecular weight can alter the properties and applications of polymers. For instance, the properties of polyethylene change substantially with polymer structure. Higher branching leads to low-density polyethylene that is suitable for film-type applications or those that require flexibility, while low branching and high molecular weight leads to high-density polyethylene, which is used for instance in containers and chairs which utilize the higher rigidity imparted by crystallinity.^{4–9}

Recent advances in controlled and reversible deactivation polymerization methods have allowed unprecedented control over primary polymer structure.^{10–14} In particular, reversible deactivation radical polymerization (RDRP) methods are among the most effective polymerization techniques for controlling the primary polymer structure. The desirability of RDRP methods arises from their ability to control the molecular weight of polymers with various functional groups, and to form complex polymers such as stars, block copolymers, and branched materials.^{10,15–18} Recently, the ability to control primary chain dispersity has emerged as an active area of research focus, with techniques that control the polymer's uniformity through catalyst control, reagent

design, reaction engineering, or blending of polymers.^{19–26} One of the simplest approaches to control the primary chain dispersity is to use reversible addition-fragmentation chain transfer polymerization (RAFT) with chain transfer agents of different activities.^{22,27,28} In RAFT, the chain transfer agent (CTA) is typically a thiocarbonylthio compound that mediates the polymerization by reacting with the propagating radical to generate the RAFT intermediate radical.^{15,27,29} This can subsequently fragment, leading to the exchange of the polymer chain capped with the CTA and the propagating polymer radical. Dispersity of the previously linear polymer, or primary chain, can be modulated in RAFT by choosing combinations of more and less active CTAs.^{15,30} The more active CTA leads to shorter transient radical lifetimes before degenerate exchange, resulting in narrower distributions, while a less active CTA causes longer transient radical lifetimes and thereby forms broader distributions.^{23,24,31} Combinations of more and less active CTAs, lead to intermediate dispersities.^{30,31}

The wealth of polymerization methods that can control dispersity, introduces the opportunity for materials properties to be engineered. Important results highlight perturbations of block copolymer self-assembly tuned by dispersity of the linear chains. This has been predicted by theoretical approaches,^{32,33} and realized through a series of detailed block copolymer selfassembly studies,^{34–36} before being translated to thermoplastic elastomers after block copolymer assembly.^{37,38} However, the effect of primary chain dispersity on covalently crosslinked networks has received limited attention, despite the fact that covalent crosslinked polymers comprise the largest fraction of thermosetting and elastomeric materials.³⁹ This implies that controlling backbone chain dispersity is an untapped resource to control bulk material properties. Recently, Weems and coworkers⁴⁰ developed a ring-opening polymerization approach to control primary backbone dispersity, with subsequent functionalization to create cross-linkable monomers. Although demonstrating changes in mechanical properties with different backbone dispersity, the materials synthesized also had substantial differences in number averaged molecular weight coupled with the changes in dispersity, making separation of the chain length and dispersity effects challenging. Similarly, Sumerlin and coworkers⁴¹ highlighted how blending polymers leading to complex molecular weight distributions with distinct dispersity and skew, lead to control over creep rates and activation energies in dynamic materials. However, the exploration of bulk mechanical properties as a function of primary chain dispersity was not performed in this study. Here, the primary chain dispersity is systematically varied using a RAFT approach, and the impact of these primary chain effects on bulk materials' mechanical properties is investigated. Additionally, taking advantage of facile processing, adhesive properties of these materials was explored. Combined, these studies highlight how systematic control over primary chain dispersity could be used in future applications that focus on polymers for structural, elastic, or adhesive applications.

Results and Discussion

Poly (hydroxyethyl acrylate) (Poly-HEA) networks were synthesized with tunable primary chain length and backbone dispersity using a modification of the mixed chain transfer agent (CTA) RAFT polymerization approach developed in the literature.^{30,31,42} A more active trithiocarbonate (TTC) CTA and a less active Xanthate (Xan) CTA were combined in different ratios to give polymers of tunable dispersity. Scheme 1A displays the synthesis of polymer networks, and Scheme 1B highlights how mixtures of more active TTC and less active Xan CTAs can give polymers of tunable dispersity. Four ratios of CTAs were used, TTC:Xan = 100:0, 67:33, 33:67 and 0:100.



Scheme 1: A) Synthesis of poly(HEA) disulfide crosslinked networks with mixed RAFT agents. B) Tuning the primary polymer dispersity using mixtures of trithiocarbonate (TTC) and xanthate (Xan) CTAs.

The mixed CTA in RAFT polymerization not only gave polymers with predictable number averaged molecular weights close to the ratio of monomer to total CTA, but also provided tunable dispersity. In all cases monomer conversion was over 95% (Figure S2). Figure 1 illustrates the molecular weight distributions for polymers targeting two distinct chain lengths: 100 (depicted in Figure 1A) and 200 (represented in Figure 1B). As indicated in Table 1, the primary chain molecular weight, determined by NMR analysis closely aligns with the primary chain molecular weight predicted by the ratio of monomers to total CTA. When employing 100% TTC, the polymers exhibit lower dispersity, ranging from 1.2 to 1.4, depending on the chain length. As the xanthate concentration increases, the dispersity gradually rises, eventually reaching ~2-3 for 100% Xan. There are some evidence of branching from SEC, especially at the higher primary chain length (Figure 1B), presumably due to the ethylene glycol diacrylate impurity that is common in HEA.⁴³



Figure 1: SEC traces of poly(HEA-EXEA) synthesized with ratios of TTC:Xan CTAs of 100:0, 67:33, 33:67 and 0:100 at a target DP of 100 (A) or 200 (B).

Table 1. Molecular weight, dispersity, thermal and tensile stress–strain data for the various synthesized poly(HEA-EXEA). ^a Young's modulus was determined from the Ogden model applied to tensile stress-strain data.

TTC:Xan	Target	$M_{ m n-Th}$	$M_{ m n-NMR}$	Đ	T_{g-DSC}	Q	σ_{peak}	Ebreak	Y
	DP	(Da)	(Da)		(°C)	(-)	(MPa)	(mm/mm)	(MPa)
100:0	100	1.31×10^4	1.37×10^4	1.17	-3±4	0.9 ± 0.1	0.29 ± 0.06	0.5 ± 0.1	0.8 ± 0.2
67:33	100	1.31×10^4	1.22×10^4	1.29	-6±8	1.31 ± 0.02	0.41 ± 0.09	0.63 ± 0.09	1.0 ± 0.2
33:67	100	1.31×10^4	$1.27 imes 10^4$	1.53	-4±2	1.45 ± 0.02	0.4 ± 0.1	0.7 ± 0.1	0.9 ± 0.1
0:100	100	1.31×10^4	$1.39 imes 10^4$	1.91	5±7	1.06 ± 0.04	0.3 ± 0.1	0.3 ± 0.1	1.5 ± 0.3
100:0	200	2.61×10^4	$2.45 imes 10^4$	1.40	-4±7	1.3 ± 0.2	0.51 ± 0.07	0.6 ± 0.1	1.3 ± 0.1
67:33	200	2.61×10^4	$2.47 imes 10^4$	1.59	0 ± 1	1.79 ± 0.06	0.7 ± 0.1	0.6 ± 0.1	1.7 ± 0.1
33:67	200	2.61×10^4	$2.48 imes 10^4$	2.09	-3±2	1.8 ± 0.1	0.8 ± 0.1	0.9 ± 0.1	1.48 ± 0.06
0:100	200	2.61×10^4	$2.39 imes 10^4$	3.05	4.0±0.3	1.28 ± 0.03	0.6 ± 0.1	0.5 ± 0.1	1.52 ± 0.04

Having established that the primary chain dispersity can be varied by mixing CTAs, the thiol groups were liberated by an amine-based deprotection, and the material was crosslinked by

taking advantage of the spontaneous transformation of thiols to disulfides in the presence of oxygen, resulting in elastomeric network materials. As seen in Table 1 and also Table S1, the materials have glass transition temperatures (T_g) at or below room temperature, consistent with soft elastomeric structures. This is reflected in the plateau modulus (E') data reported in Table S1 and Figure S4. However, neither the T_g nor the plateau rubbery modulus had any notable variability with respect to the primary chain dispersity.

The equilibrium swelling ratio (Q) was evaluated for each of the polymers synthesized and is shown in Figure 2. Interestingly, the swelling ratio reaches a peak at intermediate primary chain dispersity. Systems with either 100% TTC or 100% Xan CTA had measurably lower swelling ratios than those with intermediate dispersity, generated using either 67% TTC and 33% Xan or 33% TTC and 67% Xan ($D \sim 1.3$ -1.5 for DP 100 and 1.6-2.1 for DP 200). Single factor ANOVA was performed for each chain length. At primary chain length of 100 units, the P-value was 6×10^{-6} , and at primary chain length of 200 units, the P-value was 1×10^{-3} , for the null hypothesis that all combinations of TTC and Xan CTAs had the same swelling ratios. This statistical analysis provides very strong evidence that control over the primary chain dispersity changes the bulk material's swelling properties.



Figure 2: Swelling ratio of poly(HEA) based networks synthesized with ratios of TTC:Xan CTAs of 100:0, 67:33, 33:67 and 0:100 at a target DP of 100 (A) or 200 (B).



Figure 3: Mechanical properties of poly(HEA) based networks synthesized with ratios of TTC:Xan CTAs of 100:0, 67:33, 33:67 and 0:100. Median stress-strain curves at a target DP of 100 (A) or 200 (B). Mean peak stress (σ_{peak}) C and Mean strain at break (ϵ_{break}) D. In C and D, light-shaded bars correspond to target DP of 100, and solid bars correspond to target DP of 200.

The mechanical properties of elastomeric materials was evaluated for each chain length and backbone dispersity using tensile testing. As seen in Figure 3, the median material's stress-

strain properties depend not only on the primary chain length, but also on the backbone dispersity. Intermediate dispersity (*D*~1.3-1.5 for DP 100 and 1.6-2.1 for DP 200) led to superior mechanical properties, especially in the peak stress (σ_{peak}) compared to either low or high dispersity. Primary chain dispersity had a major impact on the σ_{peak} and to a smaller extent the strain at break (ϵ_{break}). In both the target chain length 100 and 200 systems, the σ_{peak} values were substantially higher at intermediate dispersity, formed by using either 67% of TTC with 33% Xan or 33% TTC with 67% Xan than for either the high or low dispersity materials. A similar albeit less pronounced trend was observed in ε_{break} . ANOVA indicates that both the σ_{peak} and ε_{break} are statistically significant at the 1% level for both the chain length 100 and 200 series. The P-values for equal σ_{peak} values across all dispersities are 9×10^{-3} and 3×10^{-4} for the primary chain length 100 and 200 series respectively. Similarly, the P-values for equal ε_{break} for all primary chain dispersities are 6×10^{-5} and 3×10^{-4} for the primary chain length 100 and 200 series, respectively. In general, the Young's modulus only showed a relatively minor change in properties as the primary chain dispersity was varied (Table 1). There was a systematic increase in modulus going from target chain length of 100 to 200, but beyond that however, the slope of the stress-strain curve was weakly affected by the primary chain dispersity.

Surprisingly, a network comprised of highly uniform chains does not lead to the best mechanical properties (Figure 3), nor the highest swelling (Figure 2), but instead, materials based on intermediate dispersity lead to the best network properties. This can be defined as strongest materials or materials most capable of swelling with solvent, which has been connected to overall network uniformity.^{14,44} Indeed, this is an unusual result, because in general RDRP methods lead to more uniform networks than their FRP counterparts due to the control over the primary chain structure. This highlights the importance of control over the primary chain dispersity when designing polymer materials. A possible reason for the enhanced material properties at intermediate primary chain dispersity systems have some longer chains, which can better connect distinct parts of the network together, enhancing network percolation. In contrast, lower dispersity systems have fewer opportunities for one polymer to link to several adjacent chains. In contrast, the high dispersity system has a mixture of effective long chains, but also many shorter chains that are bonded to the network, but not able to entangle or form crosslinks that percolate the network.



Scheme 2: Schematic illustration of how the network structure changes as the primary chain dispersity (Đ) increases.

Finally, the various primary chain dispersity networks were tested in adhesive applications as given in Figure 4, measured by lap shear analysis using pine substrates. When considering the target chain length of 100, the adhesive strength to pine substrates was relatively low (typically below 60 kPa), and ANOVA tests showed little variation between the polymer compositions, with a P-value of 0.32. With target chain length of 200, the adhesive strength was higher (~100 kPa) for all the samples and this resulted in greater consistency in measurement. Significantly, the moderate dispersity sample with 67% TTC had a substantially higher adhesive strength to the pine substrate, compared to all the other network structures. ANOVA testing gave a P-value of 0.056, which is close to statistically significant, and could be due to the relatively small number of replicates (triplicate for each sample). The adhesive strengths of the DP = 200 polymers are broadly consistent with the tensile analysis.

The overall results indicate that both chain length and dispersity play pivotal roles in the material properties. This is even in systems with otherwise the same crosslink density. Although chain length effects have been well reported in the literature,^{45–48} this work provides a clear indication of how primary chain dispersity can be used to increase a material's swelling, strength, extensibility and adhesive properties.



Figure 4: Adhesive strength of poly(HEA) based networks synthesized with ratios of TTC:Xan CTAs of 100:0, 67:33, 33:67 and 0:100. A) Target DP =100, B) Target DP = 200.

Conclusion

In conclusion, disulfide-crosslinked poly(HEA-EXEA) elastomers were synthesized, and the dispersity of polymer materials were tuned by mixing a more active trithiocarbonate (TTC) CTA and a less active Xanthate (Xan) CTA in different ratios. This resulted in polymers with low, intermediate and high dispersity values. The intermediate dispersity polymers showed improved mechanical properties, swelling behavior and adhesive strength compared to the low and high primary chain dispersity polymers. The polymers showed no significant differences in terms of thermal properties. Overall, this work highlights how systematic control of polymer dispersity is integral to the performance of the material in a variety of applications targeting structural, elastomeric or hydrogel type applications. Careful design of polymers with intermediate dispersity can lead to enhanced strength, swelling, and potentially tunable adhesion, superior to the extremely low or high dispersity materials.

Conflicts of Interest

The authors declare no conflicts.

Author Contributions

I.O.R. was involved in experimental design, synthesis of polymers, data analysis, visualization, writing, and editing of the manuscript. O.J.D. was involved in experimental design, validation, and analysis. N.K.S. was involved in synthesis, design of polymers, and molecular weight analysis. M.E was involved in formal and statistical analysis. K.M.M. was involved in dynamic mechanical analysis. R.W. was involved in conceptualization, editing and analysis. A.A. was involved in conceptualization, editing and analysis. D.K. was involved in conceptualization, experimental design, formal analysis, visualization and writing.

Acknowledgements

This work was supported by United States Department of Energy, Office of Science, Basic Energy Sciences, under Award No. DE-SC0018645 for network synthesis and characterization of tensile, adhesive, and swelling properties.

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