The mechanical properties of polymers are highly dependent on the mobility of the underlying chains. Changes in polymer architecture can affect inter- and intramolecular interactions, resulting in different chain dynamics. Herein, an enhancement in the mechanical properties of poly(butylmethacrylate) is induced by folding the polymer chains through covalent intramolecular crosslinking (CL). Intramolecular CL causes an increase in intramolecular interactions and inhibition of intermolecular interactions. In both the glassy and rubbery states, this molecular rearrangement increases material stiffness. In the glassy state, this molecular rearrangement also leads to reduced failure strain, but surprisingly, in the rubbery state, the large strain elasticity is actually increased. An intermediate intramolecular CL degree, where there is a balance between intra- and intermolecular interactions, shows optimal mechanical properties. Molecular dynamics simulations are used to confirm and provide molecular mechanisms to explain the experimental results.

1. Introduction

Controlling macroscopic properties by judicious design and control of the molecular structure has been a key driving force behind the development of new polymer architectures. New strategies to improve the thermomechanical properties of plastic materials that do not involve irreversible covalent crosslinks (CL) have been extensively studied and reported in the literature. For example, changes in chain architecture to make branched [1] and star polymers, [2] or even a combination of both [3] have been shown to have a profound influence on the mechanical performance. For instance, the elongation at break of highly branched star polymers was found to be greater than that of the linear architecture. Another approach is to create networks by the incorporation of non-covalent CL such as hydrogen [4–6] or coordinative bonds between chains. [7–9] A promising new strategy that is explored in this manuscript, is balancing the inter- and intramolecular interactions through the use of chemical bonds to fold polymer chains, forming an architecture commonly known as single chain polymer nanoparticles (SCPNs). [10–12] Recent research on these interesting macromolecules has significantly advanced the possible chemistries used for SCPN synthesis [13–16] and elucidated the effect of solvents and concentrations in controlling the particle size and shape. [17–19] Folding a polymer chain to a less dynamic structure can be useful in a variety of applications as the macromolecule physical properties and their interactions are significantly affected, while the polymer chemistry remains mostly unchanged. [20–22] Many studies have characterized SCPN molecular level behavior in solution, [22–26] in addition to a few melt studies which looked at the interactions between the folded chains. [21,27] Finally, more recently, we have conducted experimental and theoretical studies to better understand the influence of intramolecular CLs in the solid state, looking at mechanical and thermomechanical behavior of SCPNs assembled into bulk thermoplastic materials. [28,29] Our initial studies focused on the effects of intramolecular CLs below the glass transition temperature (Tg) such as reducing chain entanglement and decreasing ductility. Here, we exploit the effect of intramolecular CLs on bulk materials assembled from SCPNs composed primarily of polybutylmethacrylate (PBMA), as properties can be studied both below and above Tg. In order to understand the underlying mechanisms by which intramolecular CLs influence macroscale thermomechanical properties, we investigate these materials with different extents of CL. In addition to mechanical testing on the synthesized materials, we adopted molecular dynamics (MD) simulations and carried out simulated mechanical testing on the same class of material to take a closer look at microstructural aspects such as the size, shape, and response to deformation of individual molecules in a bulk polymer. MD enables us to investigate at a scale that would be difficult if not impossible experimentally.

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2. Results and Discussion

2.1. SCPNs Synthesis and Characterization

Given that one goal of this research is to test materials in both the rubbery and glassy states, polymers based on butyl methacrylate were prepared. PBMA has a relatively low \( T_g \) of 20 °C\(^\text{[30]} \) and is an easy-to-work solid. The synthetic strategy is based on the method developed by Pomposo et al.\(^\text{[14]} \) which uses Michael addition for a CL reaction. The CL degree for each polymer was calculated by \(^{13}\text{C}-\text{NMR} \) [see the Supporting Information (SI)]. The four SCPNs synthesized are marked from E1, with the lowest degree of intramolecular CL to E4, with the highest degree. The MD simulated SCPN were formed from polyethylene (PE)-like chains following the procedure from our prior work.\(^\text{[31]} \) The bulk polymers were modeled as assemblies of 27 SCPN equilibrated under periodic boundary conditions (see SI). The four MD simulated SCPNs are marked from M1, with the lowest degree of intramolecular CL to M4, with the highest degree.

The size of the individual, independent SCPNs reflects the CL density, synthesis/simulated synthesis conditions, and the current environment. All synthesized polymers were characterized by triple-detector gel-permeation chromatography (GPC) (Table 1, and Figure S1, SI), which showed the expected increase in retention time as CL degree increases, indicating a decrease in hydrodynamic volume of individual, independent SCPNs (\( R_g \)). \( R_g \) is measured in a dilute solution, where the individual macromolecules are able to swell and do not interact with other macromolecules, therefore the effect of intramolecular CL is significant only at high CL degree (E4). Another hint into the shape and size of individual, independent SCPNs comes from our previous MD studies on individual SCPNs in vacuum, where the radius of gyration (\( R_g \)) was found to be nearly independent of the CL degree with only a slight reduction.\(^\text{[31]} \) \( R_g \) indicates how constituent monomers are distributed about the center of mass of the chain. A larger \( R_g \) corresponds to a more unfolded molecule. The trend in vacuum does not imply that the size is independent of CL degree in the presence of solvents, as already observed in decreasing \( R_g \) in experiment, or neighboring macromolecules in MD studies (in bulk polymer).

In bulk polymers, SCPNs are not isolated anymore but surrounded by other similar SCPNs. Therefore, it is crucial in this study to understand the size and shape of individual SCPNs in the bulk, which is a challenge experimentally, but relatively straightforward by means of MD simulation. We measured by MD simulation the \( R_g \) of individual SCPNs in the bulk in the current study and found that the \( R_g \) decreases with increasing CL degree from linear to 20% as shown in Figure 1. Interestingly, the \( R_g \) of SCPNs in the presence of other macromolecules converge to those of individual, independent SCPNs (ca. 18 Å) in vacuum as the CL degree increases. This implies that SCPNs are less unfolded with increasing CL degree. The lesser extent of chain unfolding is also observed in molecular snapshots (see Figures S20–S28, SI).

2.2. Glass Transition Temperature

The glass transition temperature was measured using differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) to provide some experimental indications on the effect of intramolecular CL on segmental dynamics. In agreement with ours and others previous results,\(^\text{[15,28,29,32,33]} \) \( T_g \) increases in PBMA with increasing CL degree (Table 1). \( T_g \)’s determined by MD simulations found the same trend (Table 2). The increase in \( T_g \) with increasing CL degree is attributed to reduced mobility due to chain confinement as previously demonstrated in non-SCPN systems.\(^\text{[34,35]} \) It is important to mention that the difference in absolute \( T_g \) values obtained from experiment and MD simulations results is due to the difference in polymer chemistry.

2.3. Monotonic Uniaxial Tensile Tests

In order to investigate temperature-/state-dependent mechanical properties, uniaxial tension tests were conducted at a nominal strain rate of 0.001 s\(^{-1}\) both at room temperature (below \( T_g \)) and 80 °C (above \( T_g \)). MD simulations of uniaxial tension tests were conducted above and below \( T_g \) at a nominal strain rate of 10\(^8\) s\(^{-1}\). For both the experiments and simulations, we express these results in terms of true stress and strain (see SI).

At room temperature, EL, E1, and E2 deform and present strain hardening, however, E3 and E4 fail before any plastic deformation occurs (Figure 2a). Elastic modulus was extracted from these curves (Figure 2b). Unexpectedly, unlike our previous study using PMMA SCPNs in which the elastic modulus was not affected by CL degree,\(^\text{[28]} \) significant changes are seen in PBMA SCPNs. This difference in the mechanical response at

Table 1. Experimental properties of linear and intramolecular CL polymers.

<table>
<thead>
<tr>
<th>Type</th>
<th>CL degree(^a) [%]</th>
<th>( T_g ) (DMTA)(^b) [°C]</th>
<th>( T_g ) (DSC)(^c) [°C]</th>
<th>( M_e )(^d) [kDa]</th>
<th>( R_g ) (w)(^e) [nm]</th>
<th>([\eta] w )(^f) [mL g(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EL</td>
<td>0</td>
<td>55</td>
<td>29</td>
<td>111.8</td>
<td>8.8</td>
<td>34.3</td>
</tr>
<tr>
<td>E1</td>
<td>2</td>
<td>57</td>
<td>37</td>
<td>125.1</td>
<td>8.8</td>
<td>32.9</td>
</tr>
<tr>
<td>E2</td>
<td>3.5</td>
<td>67</td>
<td>43</td>
<td>152.0</td>
<td>8.9</td>
<td>29.8</td>
</tr>
<tr>
<td>E3</td>
<td>6</td>
<td>70</td>
<td>47</td>
<td>145.0</td>
<td>8.7</td>
<td>27.7</td>
</tr>
<tr>
<td>E4</td>
<td>9</td>
<td>70</td>
<td>50</td>
<td>171.3</td>
<td>8.1</td>
<td>22.9</td>
</tr>
</tbody>
</table>

\(^a\)Calculated from \(^{13}\text{C}-\text{NMR}; \(^b\)\( T_g \) corresponds to glass transition temperature, measured as maximum \( \tan \delta \) at 1 Hz; \(^c\)Midpoint; \(^d\)\( M_e \) corresponds to polymer molecular weight molar mass, \( R_g \) is the hydrodynamic radius, and \([\eta] w \) is the intrinsic viscosity. Parameters where calculated from three-detector GPC.
Table 2. Glass transition temperature, density, degree of entanglement, and elastic modulus of SCPNs as a function of CL degree of the MD material models.

<table>
<thead>
<tr>
<th>Type</th>
<th>CL degree [%]</th>
<th>$T_g$ [°C]</th>
<th>$\rho$ at the glassy state [g \text{ cm}^{-3}]</th>
<th>$N_e^{\text{eq}}$ at the glassy state</th>
<th>Elastic Modulus at the glassy state [GPa]</th>
<th>$\rho$ at the rubbery state [g \text{ cm}^{-3}]</th>
<th>$N_e^{\text{eq}}$ at the rubbery state</th>
<th>Elastic Modulus at the rubbery state [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML 0</td>
<td>0</td>
<td>−53.98</td>
<td>0.927</td>
<td>76.7 ± 0.4</td>
<td>3.266</td>
<td>0.852</td>
<td>70.9 ± 3.1</td>
<td>0.376</td>
</tr>
<tr>
<td>M1 5</td>
<td></td>
<td>−36.10</td>
<td>0.941</td>
<td>572.9 ± 7.2</td>
<td>3.533</td>
<td>0.876</td>
<td>442.7 ± 50.7</td>
<td>0.621</td>
</tr>
<tr>
<td>M2 10</td>
<td></td>
<td>−31.65</td>
<td>0.956</td>
<td>982.9 ± 19.5</td>
<td>4.083</td>
<td>0.902</td>
<td>870.0 ± 84.7</td>
<td>1.082</td>
</tr>
<tr>
<td>M3 15</td>
<td></td>
<td>−26.42</td>
<td>0.976</td>
<td>999.0 ± 0.0</td>
<td>4.433</td>
<td>0.924</td>
<td>999.0 ± 0.0</td>
<td>1.739</td>
</tr>
<tr>
<td>M4 20</td>
<td></td>
<td>−27.58</td>
<td>0.939</td>
<td>999.0 ± 0.0</td>
<td>4.130</td>
<td>0.905</td>
<td>999.0 ± 0.0</td>
<td>2.160</td>
</tr>
</tbody>
</table>

$N_e$ corresponds to the number of monomers between entanglements (see SI, the details on entanglement).
Figure 2. a) Stress–strain behavior and b) elastic modulus as a function of CL degree at room temperature from experiment. c) Stress–strain behavior and d) change in radii of gyration as a function of CL degree at the glassy state from MD simulations. The solid, dashed, and the dotted lines correspond to \(R_g, R_g, R_g\), and the affine deformation, respectively.

Figure 3. a) Stress–strain behavior and b) elastic modulus as a function of CL degree at 80 °C from experiment. c) Stress–strain behavior and d) change in radii of gyration as a function of CL degree at the rubbery-like state from MD simulations. The solid, dashed, and the dotted lines correspond to \(R_g, R_g, R_g\), and the affine deformation, respectively.
other more. The more rigid the SCPNs, the more likely this sliding is to cause the material to fail. This trend towards brittle behavior is quite apparent in our room temperature experiment in that failure strain decreases with increasing CL degree. At 80 °C experimentally, all of the materials are quite stretchable, and the deformation mechanism of sliding does not seem to be SCPN deformability limited.

Again, it is important to note that the chemistry is different between experiment and simulation. We adopted PBMA for the experiments and a PE-like polymer for MD models, but the synthesized materials and MD models both consist of assemblies of polymer chains with intramolecular CL. Overall both the synthesized materials and MD models present increase in strength and stiffness compared to the linear polymer. MD simulations provide additional information regarding the changes in density and $R_g$ during deformation which cannot be measured experimentally.

### 2.4. Cyclic Uniaxial Tensile Tests

In order to better understand the variation in stress response due to difference in chain configuration caused by intramolecular CL, cyclic uniaxial tensile tests were carried out at 80 °C for each polymer. The cyclic test used in this case consists of three rounds of strain and release in sequence, up to six increasing strain levels at a nominal strain rate of 0.001 s$^{-1}$. Figure 4a,d shows representative results from EL and E3 (see SI for measurements for all additional polymers). The shapes of the curve for both polymers can be broadly described by the same features from each initial unload, there is a substantial residual strain at zero force and a large hysteresis; upon each reload the peak stress is slightly reduced compared to the previous repeat; overall the stress is reduced compared to the corresponding monotonic test. Comparing EL and E3, it is apparent that E3 has less residual strain and greater hysteresis on the second and third repeats at each strain. To better quantify the differences between EL and E3, properties extracted from this test are plotted as a function of cycle number in Figure 4.

The normalized moduli extracted from unloading at each strain and repeat are presented in Figure 4b,e. While stiffness fluctuates for EL, for E3 it increases with strain. This increase in E3 modulus is likely due to improved alignment and packing of SCPNs with the stress vector while maintaining the individual SCPN stiffness. Correspondingly, the stress increases with strain for E3, whereas it levels off and even decreases over the same range for EL.

The viscous nature of each polymer is apparent through the reduced stress with each reload to a given strain, the strain when force becomes zero upon unloading and non-zero upon reloading, and the strain energy dissipated with each cycle (hysteresis). Each of these indicators shows that EL acts in a much more fluid-like manner than E3. The peak stress of EL drops dramatically from repeat one to two and then again from two to three, showing that the polymer has shifted to a new quasi-equilibrium configuration based on prior peak strain; the peak stress for E3 only drops by a few percent at each repeat, although this drop does become more pronounced at larger strains (Figure S17a,d, SI). In Figure 4c,f, the total height of blue and red bars corresponds to strain energy density (SED) on loading, the blue portion is recovered, and the red portion is dissipated. Both polymers recover and dissipate less energy after each repeat. EL presents a significant energy reduction after the first repeat for each cycle, and the repeats have little effect. In contrast, for E3, the recovered and dissipated energy only reduces slightly for repeats, and is a function of maximum
strain. At first glance, this experimental result seems contradictory with the MD finding that SCPNs have more relative chain motion (viscous flow) than ML, however as showed in our previous work,[29] the greater the CL degree, the greater the stress for deforming the SCPN a given amount—since this individual SCPN deformation is reversible, this factor has a strong effect on the dissipation to recovery ratio.

2.5. Intermolecular Interaction

Individual SCPNs themselves deform or slide past each other in response to macroscale deformation. In our prior work, we found that loss of entanglements in high CL density SCPN assemblies was responsible for the loss of ductility in the glassy state, however this is clearly not a dominant factor in the rubbery state because the high CL polymers can stretch greater than 1400%. Therefore in this subsection, we explore the influence of intermolecular non-covalent interactions beyond entanglements on the deformation mechanisms. Experimentally, it is incredibly difficult to isolate the effects of intermolecular non-covalent interactions from SCPN rigidity and entanglements, but MD simulations enable us to modulate these effects independently. We reduced the strength of the intermolecular non-covalent interactions (between monomers in different SCPNs), while keeping the intramolecular non-covalent interactions (between monomers within SCPNs) and the SCPN rigidity the same (see SI for modulating intermolecular non-covalent interactions). Then, monotonic uniaxial tension at a strain rate of $10^8$ s$^{-1}$ was applied and both the stress response and deformation of the individual SCPNs were examined. At the glassy state, where monomers/chain segments are likely frozen and SCPNs are more rigid, as the strength of intermolecular non-covalent interactions are reduced, a substantial drop-off in both strength and fracture strain are seen as shown in Figure 5a, which shows the stress–strain behavior of M1 with varying strength of intermolecular non-covalent interactions (see Figures S34–S38, SI for different CL degrees). Despite the difference in macroscale behavior, surprisingly there is almost no change in how individual SCPNs deform ($R_g$) until just before failure (Figure 5b). At the rubbery-like state, where chain segments have more mobility and the SCPN are less rigid, the stiffness of the material decreases significantly with decreasing strength of intermolecular non-covalent interactions as shown in Figure 5c (see Figures S39–S43, SI for additional cases). This reduced stress is a consequence of the reduced deformation of SCPNs as apparent in the $R_g$ plot (Figure 5d). It is clear that even aside from entanglements, non-covalent interactions among SCPNs are critical for transmitting macroscale deformation and maintaining material cohesion. Coming back to the experimental results, there is a trade-off with increasing CL degree between stiffer and stronger individual SCPN and loss of intermolecular non-covalent interactions; E3 seems to

![Figure 5](image.png)

Figure 5. The behavior of type M1 with varying strength of intermolecular non-covalent interactions (see SI for the behavior of different types). a) Stress–strain behavior and b) change in radii of gyration at the glassy state from MD simulations as a function of the ratio of the strength of intermolecular non-covalent interactions to that of intramolecular ones. c) Stress–strain behavior and d) change in radii of gyration at the rubbery-like state from MD simulations as a function of the strength ratio. 1, 0.9, and 0.75 represent three different ratios and the smaller the value, the weaker the strength of intramolecular non-covalent interactions (see SI for modulating intermolecular non-covalent interactions). In both b) and d), the solid, dashed, and the dotted lines correspond to $R_g$, $R_{L_r}$, and the affine deformation, respectively.
be closest to the balance point for these two factors among the CL densities examined here.

3. Conclusions

We have studied the thermomechanical properties of bulk polymers assembled purely from PBMA SCPNs to understand the effect of intramolecular CL on the material behavior of rubbery polymers. Similar to PMMA-based SCPN, the \( T_g \) increases as a function of intramolecular CL degree. Yet, in contrast with these PMMA studies, we found that maximum stiffness and strength are improved at a moderate intramolecular CL degree (E3) in the glassy state and that stiffness and toughness are improved in the rubbery state. Cyclic tests revealed that the viscous nature of the base linear polymer is reduced by the addition of intramolecular CL. Both strain recovery and SED recovery fraction are increased with the addition of CLs.

Our results indicate that the presence of intramolecular CL can significantly improve the mechanical properties of bulk polymers at the rubbery state. The main effect of these additional bonds is in resisting unfolding under applied stress. These intramolecular covalent bonds are most effective macroscopically when there are still intermolecular interactions between chains from entanglements or even close packing of the SCPN. This study adds to the concept of using folded polymers to make bulk materials and perhaps, provide improved materials. Further study is underway to further understand the role of the non-covalent intermolecular interactions in these materials.

4. Experimental Section

Materials: All chemicals, unless otherwise stated, were purchased from commercial sources and utilized without further purification. Butyl methacrylate (BMA) was filtered through basic alumina to remove hydroquinone monomethyl ether (MEHQ) inhibitor. The purified BMA was kept in a refrigerator in a closed flask under argon.

Butyl methacrylate (BMA) was filtered through basic alumina to remove hydroquinone monomethyl ether (MEHQ) inhibitor. The purified BMA (100 mL, 0.63 mol), AEMA (21 mL, 0.12 mol), 2-cyanoprop-2-yl-dithiobenzoate (CPDB) (125 mg, 0.56 mmol) and 2,2-azobis(2-methylpropionitrile) (AIBN) (21.85 mg, 0.13 mmol) were dissolved in ethyl acetate (100 mL). The reaction mixture was treated with three freeze-pump-thaw cycles and kept in a refrigerator in a closed flask under argon.

Azobisisobutyronitrile.

\( \text{BMA} + \text{AEMA} \xrightarrow{\text{CPDB, AIBN}} \text{SCPN} \)

\( \text{KOH, THF, rt} \)

\( \text{Scheme 1. Synthesis of linear polymer and SCPNs. CPDB = 2-cyanoprop-2-yl benzothioate. AIBN = Azobisisobutyronitrile.} \)
backbone. The bulk polymer is constructed from 27 SCPN and each SCPN exhibits one of three intramolecular CL distributions.[10] All MD simulations were carried out using the large-scale atomic/molecular massively parallel simulator (LAMMPS) on the Extreme Science and Engineering Discovery Environment Stampede 2 cluster.[18,19] The SCPN bulk systems with different CL degrees (M1: 5%, M2: 10%, M3: 15%, and M4: 20%) and the linear bulk system (ML) for reference were equilibrated through multistep equilibration including simulated annealing. The equilibrated systems are used to investigate glass transition temperature by simulated cooling,[20,21] stress–strain response by simulated uniaxial tension at a strain rate of $10^4$ s$^{-1}$, chain entanglement by primitive path analysis,[22,23] and SCPN shape change during uniaxial tension by radius of gyration.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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