Mechanical and Thermomechanical Characterization of Glassy Thermoplastics with Intrachain Cross-Links

Or Galant,[†] Suwon Bae,[‡] Feng Wang,[†] Avishai Levy,[†] Meredith N. Silberstein,*[,‡] and Charles E. Diesendruck*[,†,§]

[†]Schulich Faculty of Chemistry, Technion — Israel Institute of Technology, Haifa 3200008, Israel

[‡]Department of Mechanical and Aerospace Engineering, Cornell University, Ithaca, New York 14853, United States

[§]Russell Berrie Nanotechnology Institute, Technion — Israel Institute of Technology, Haifa 3200003, Israel

Ⓢ *Supporting Information*

ABSTRACT: The mechanical properties of an amorphous polymer are a consequence of the inter- and intramolecular interactions which are typically similar. Yet, polymers can be made with covalent intramolecular cross-links, leading to stronger intramolecular interactions. Here, a study on the effect of this intramolecular cross-linking on the mechanical properties of a glassy polymer is shown. A linear poly(methyl methacrylate) with defined size was cross-linked at different ratios and assembled into solid samples by solvent casting. Mechanical testing indicates that intramolecular cross-linking does not affect the mechanical properties at the elastic region but does influence these properties at the plastic region. Interestingly, intramolecular cross-linking leads to different effects than "regular" interchain cross-linking. The results are consistent with a reduction in chain entanglement, reducing toughness and to a lesser extent strength.

INTRODUCTION

Polymers are either thermoplastics or thermosets[1] according to their thermal response, which are a direct consequence of the polymer chain architecture. Unlike thermosets, thermoplastics are materials in which the chains are not cross-linked to each other. Consequently, thermoplastics are thermoformable, and this formability is repeatable. Thermosets, conversely, are not meltable or soluble and therefore cannot be thermally processed or dissolved. Thermoplastics present both a glass transition temperature (T_g) and a melting point (T_m), whereas thermosets are linked between the chains by chemical bonds; therefore, they present only a T_g above which there is a relative movement between the chains. However, these movements are restricted by the cross-links, and therefore they do not melt.

Classical thermoplastics have linear polymer chain architectures and present properties that depend on the molecular weight and monomer chemistry.[2] The development of new polymer architectures allows tailoring of polymer properties without changing the monomer chemistry. A significant example is the development of hyperbranched polymers,[3] which can be characterized as "thermoplastics", but differ significantly in properties from linear polymers of the same chemical composition due to disruption of intermolecular forces and changes in shape.

Likewise, SCPNs (single chain polymer nanoparticles) are thermoplastic polymers that present similar chemical composition to linear polymers but have a different architecture.[4] SCPNs are prepared by intramolecular chemical cross-linking

of various positions along linear polymer chains. The original idea of collapsing a polymer chain with chemical bonds was proposed and studied theoretically by Kuhn in 1956,[5] who also fulfilled the first experimental example in 1962.[6] This polymer architecture became important as a synthetic approach to produce tiny organic nanoparticles (from 1.5 to 20 nm) that could not be obtained by emulsion polymerizations.[7−11] The effect of cross-link density on properties of the individual particles such as shape,[12,13] size,[13−19] rigidity,[8,12,20] and intrinsic viscosity[14,16,21] have been largely studied. We recently published a molecular dynamics study of the thermomechanical properties of individual SCPNs as a function of cross-link density.[20] For individual SCPNs, increasing cross-link density does not affect glassy state stiffness, mildly increases strength, and decreases subchain mobility. Yet, to our knowledge, experimental investigations on the mechanics of SCPNs have been limited to blends with linear polymers or as rheology modifiers in solution.[22,23] While nanoparticles have long been used as fillers to improve bulk mechanical properties,[24,25] investigation of bulk materials prepared from pure assemblies of SCPNs has not yet been studied. Here, we exploit synthetic control over individual SCPN properties and study how those changes affect interparticle interactions, leading to the ability to tune some mechanical and thermomechanical properties in a

A

Scheme 1. Synthesis of Linear Polymer and SCPNs (CPDB = 2-Cyanopropan-2-yl Benzothioate; AIBN = Azobisisobutyronitrile)
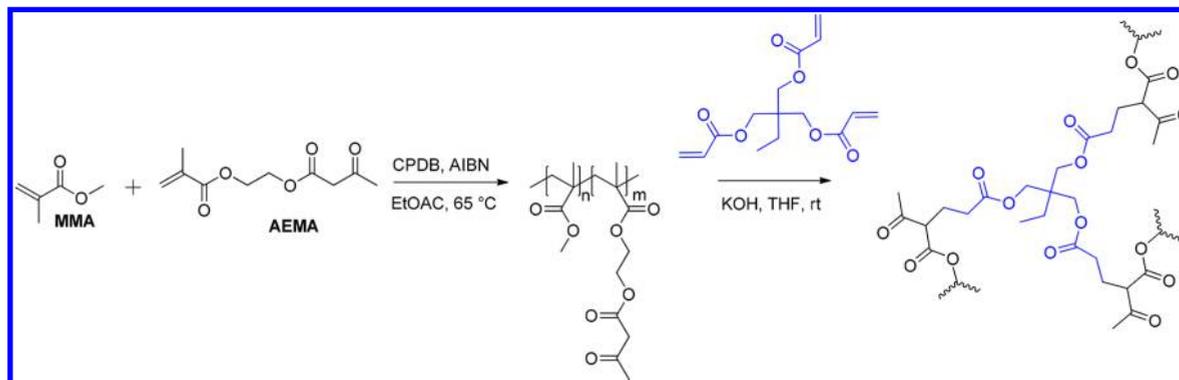
bulk glassy polymer. More specifically, we use polymers having the same degree of polymerization (DP), vary the cross-link density, and characterize the mechanical and thermomechanical properties of the bulk assembly thermoplastic.

■ EXPERIMENTAL SECTION

Materials. All chemicals, unless otherwise stated, were purchased from commercial sources and utilized without further purification. MMA was filtered through basic alumina to separate from inhibitor MEHQ. The filtered MMA was bubbled with argon for 15 min.

Synthesis of Polymer and SCPNs. The polymers were prepared following previously described procedures.[26,27] The synthetic strategy involves a two-step approach as can be seen in Scheme 1. First, RAFT (reversible addition–fragmentation chain transfer) polymerization was used to prepare a linear random copolymer containing a mixture of methyl methacrylate (MMA) and (2-acetoacetoxy)ethyl methacrylate (AEMA). This polymer was characterized and used as the linear precursor in our study. A small peak in low retention shoulder is observed presenting twice the M_w of the main peak, representing a small amount of radical coupling termination (Figure 1). Parts of this

Figure 1. Change in the GPC as a function of intramolecular cross-link density (refractive index detector shown).

polymer underwent intramolecular cross-linking by Michael addition using different amounts of trimethylolpropane triacrylate (TMT) as the Michael acceptor to form polymers with different cross-link density but all containing the same DP.

Film Preparation. Films were prepared by film casting on a Teflon-coated Petri dish with 50 mm diameter. The dissolved polymer (800 mg) in 1,4-dioxane (8 mL) was left overnight in the Petri dish for slow evaporation inside a hood. The films were cut to the desired shape using an "Epilog Zing" 24 laser cutter. The specimens for tensile tests were laser cut according to ASTM D638-14 dimensions. The specimens were then dried under high vacuum overnight. Specimens' dimensions were measured using a digital calliper and a micrometer at
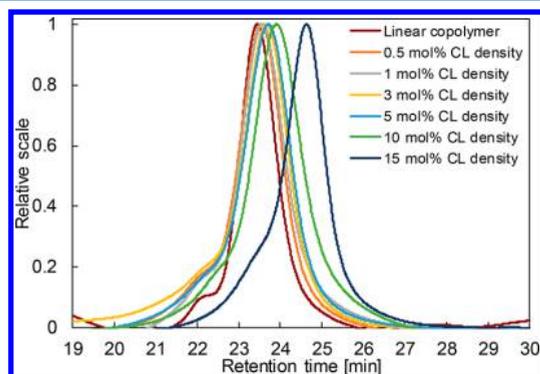
three different locations along the gauge length and averaged. The specimens for DMA were laser cut into rectangles 4.5–5 mm in width, 20 mm in length, and 0.25–0.5 mm in thickness.

Characterization. GPC analyses were done in a Thermo LC system equipped with TSKgel Guard Column HHR-L and 4 TSKgel G4000HHR columns in sequence. Detection was obtained with a pentadetector system including Dionex DAD-3000 PDI UV–vis Detector, Wyatt Viscostar II, Wyatt OPTILAB T-rEX, Wyatt MALS DAWN HELEOS II 8+TR, and WyattQELS DLS. GPC data analysis was done using Wyatt's Astra 6 software. Dynamic mechanical analyses were done in a DMA Q800 (TA Instruments) using 4 mm single cantilever configuration. DMA data were analyzed by the TA Universal Analyzer Program. Tensile tests were done using a "Zwick" Z010, and strain was calculated by digital image correlation (DIC) using VIC-2D. From initial testing, we found a significant disparity between the strain rate calculated from the gauge length given by the ASTM standard. The effective gauge length of 20.1 mm was therefore estimated by a finite element simulation (Abaqus) of the specimen under uniaxial deformation assuming linear elastic behavior. The experimentally realized strain rate observed by DIC was 70–90% of the target strain rate. DSC analyses were done in a Mettler Toledo DSC-1 and analyzed by STARe software. All ^{1}H and ^{13}C NMR spectra were recorded using an AVANCE II 200, 300, or 400 MHz (CDCl$_3$, δ) Bruker spectrometer at the Technion NMR facilities.

■ RESULTS AND DISCUSSION

SCPNs Synthesis and Characterization. For this research, we decided to prepare a series of materials based on glassy PMMA with 0–15 mol % degree of cross-linking. The method developed by Pomposo et al.,[27] which uses Michael addition for cross-linking was chosen. This method presents the advantage of having similar and compatible chemistry between the monomers and cross-linkers. In addition, since the polymerization rate of the two monomers—AEMA and MMA—are similar, a random copolymer distribution is obtained. As a result, the amount of intramolecular cross-linking can be controlled, but their positions are random. The use of RAFT polymerization provides a linear copolymer precursor with low dispersity,[28] leading to SCPNs that differ in the degree of cross-linking but present similar DP. The cross-link density described in this article assumes 100% conversion from the addition of TMT, but more realistic values were measured by NMR for the samples with higher cross-link densities (see Supporting Information).

All synthesized polymers, linear and intramolecularly collapsed, were initially characterized and compared by triple-detector GPC (Figure 1 and Table 1). As the chain cross-link density is increased, the polymer peak moves to higher retention times, indicating a decrease in size. The average

Table 1. Polymers Used in This Study and Their Properties from Triple-Detector GPC

| cross-link density[a] [mol %]	M_n[b] [kDa]	$Đ$[b]	R_h[b] [nm]	$[\eta]_0$[b] [mL g^{-1}]
0	102.4	1.08	7.8	30.3
0.5	105.6	1.09	7.8	28.4
1	105.7	1.10	7.8	28.7
3	117.1	1.12	7.7	24.8
5	116.4	1.11	7.3	22.1
10	117.8	1.08	7.1	19.7
15	117.0	1.13	6.5	15.1

[a]Calculated from relative amount of TMT added. [b]Calculated from triple-detector GPC.

molecular weight increases slightly because of the use of an external cross-linker that adds to the weight of the polymer chain. The reductions in intrinsic viscosity and hydrodynamic radius (R_h) are characteristic of intramolecular collapse. It can be seen from Table 1 that for slightly collapsed chains the change in hydrodynamic radius and intrinsic viscosity is not significant, but as the chain is more heavily cross-linked there is a great decrease in these properties.

Tensile Tests. Mechanical testing of all the materials was carried out using tensile testing. The tests were conducted on dogbone specimens at room temperature at a nominal strain rate of 0.001 s^{-1}. All tested polymers present T_g well above room temperature (see below) and are therefore in the glassy state during these tests. Linear polymer and 15 mol % cross-linked SCPNs were characterized by SAXS and WAXS (see

Supporting Information), and no areas of crystallinity were observed, indicating that the polymers remain amorphous even with large intramolecular cross-link density. Engineering stress was calculated using force data with the average area measured at three points along the gauge section. Engineering strain was calculated from the gauge length extension determined by digital image correlation. The results are summarized in Figure 2; however, for the 15 mol % intrachain cross-link density, the specimens were too brittle and therefore not enough data were collected to obtain suitable results. The linear to 10 mol % intrachain cross-link density specimens all exhibit some plasticity with some specimens breaking just at the yield peak and others softening before fracture.

The elastic response (Figure 2b) does not change as a consequence of intramolecular cross-linking. Commercial PMMA has an elastic modulus of 1.8−3.1 GPa.[29] Our house-made polymers presented elastic moduli varying between 1.41 and 1.79 GPa, but the apparent differences fall within the error and therefore are not statistically different; i.e., the addition of covalent intramolecular bonds has no significant effect on this property in glassy materials. Since the linear polymers in the glassy state present strong supramolecular interactions between chains, changing a few of these interactions from supramolecular to covalent does not significantly affect the structure or dynamics of the chains in the elastic region. Although the amount of entanglement between chains should differ between SCPNs and linear polymers, this difference is not reflected at small deformation.
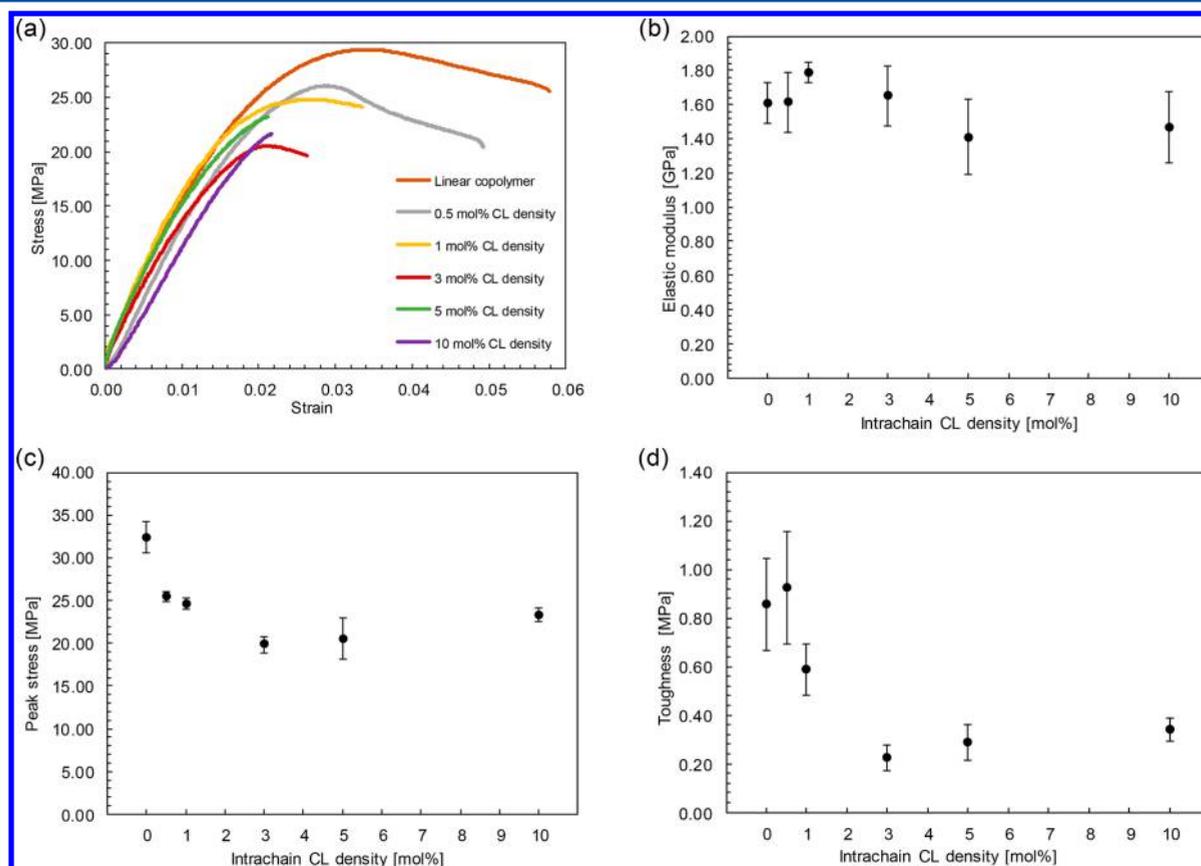
Figure 2. Engineering stress−strain curves (a). Change in elastic modulus (b) in peak stress (c) and in toughness (d) as a function of intramolecular cross-link density. Average values from 3 to 5 measurements and their standard divisions are shown.

Conversely, the intramolecular collapse does affect properties in the plastic region. For example, the peak stress (Figure 2c), which reflects the strength of the material, decreases from 32.39 ± 1.85 MPa for the linear polymer to 25.49 ± 0.61 and 24.63 ± 0.70 MPa for 0.5 and 1 mol % cross-link density polymers, respectively, a ca. 28% decrease. At 3 and 5 mol %, there is an additional 25% reduction in peak stress. Samples made from SCPNs with 10 mol % cross-link density polymer are not statistically different despite the small increase in peak stress.

Specimen toughness was calculated from the area under the engineering stress–strain curves (Figure 2d). Small amounts of cross-linking (0.5 and 1 mol %) did not statistically affect toughness, but further cross-linking led to a significant reduction in toughness. The difference between samples was very clear even when handling samples manually—samples made from SCPN with high cross-link density were quite brittle, much more than the linear polymer and the slightly intrachain cross-linked samples. The toughness for the linear copolymer, 0.5 and 1 mol % intrachain cross-linked samples, ranged between 0.59 and 0.92 MPa with values that are not statistically different. On the other hand, the toughness measurements for samples made from 3, 5, and 10 mol % cross-linked polymers are much lower, ranging from 0.22 to 0.34 MPa, approximately 1/3 of the linear precursor toughness.

For linear thermoplastic polymers, the noncovalent interactions between chains provide stiffness, while disorganized entanglements among chains provide toughness. Therefore, chain entanglements affect the mechanical properties of the bulk polymer in the plastic region, whereas in the elastic region they do not have any significant effect. When deformation occurs under uniaxial stress, entanglements resist chain stretch and movement. Increasing the cross-link ratio for a polymer with similar DP collapses the chains into smaller particles with increased intramolecular interactions, and therefore there are less potential for interchain entanglements, as well as the interactions between chains. As a result, when stress is applied, chains detach from each other more easily. Therefore, the stiffness of the polymer is not affected by intramolecular cross-linking in the glassy state; however, the polymer becomes less strong and drastically more brittle. The slight decrease in strength is likely a competition between the increase in individual SCPN strength and the decrease in entanglements between SCPN.

Interestingly, it has been shown that intermolecular cross-linking of PMMA also does not affect the elastic modulus. However, contrary to intramolecular cross-linking, intermolecular cross-linking increases the toughness, as deformation before failure increases.[30] Therefore, the architectural change of connecting monomers from the same polymer chain causes an opposite trend in the plastic region as compared to traditional cross-linking.

Dynamic Mechanical Analysis. In addition to tensile testing, thermomechanical measurements were carried out in dynamic mechanical analysis using a single-cantilever configuration. A monotonic strain test with the linear copolymer was run at room temperature to define an appropriate strain ratio in the elastic region. From this test, 0.05% was chosen as appropriate strain for temperature sweep measurements. DMA temperature sweeps were conducted at 1 Hz and 0.05% strain. The specimen was held at 50 °C for 10 min, and then the temperature was raised at 2 °C min^{-1} up to 150 °C. Additionally, we defined a minimum force 0.005 N; i.e., when

this minimum force was reached, the force was kept constant and the strain was increased.

Representative storage modulus and tan δ for linear copolymer and 5 mol % intrachain cross-linked samples are shown in Figure 3a. The test started below T_g, ran until it
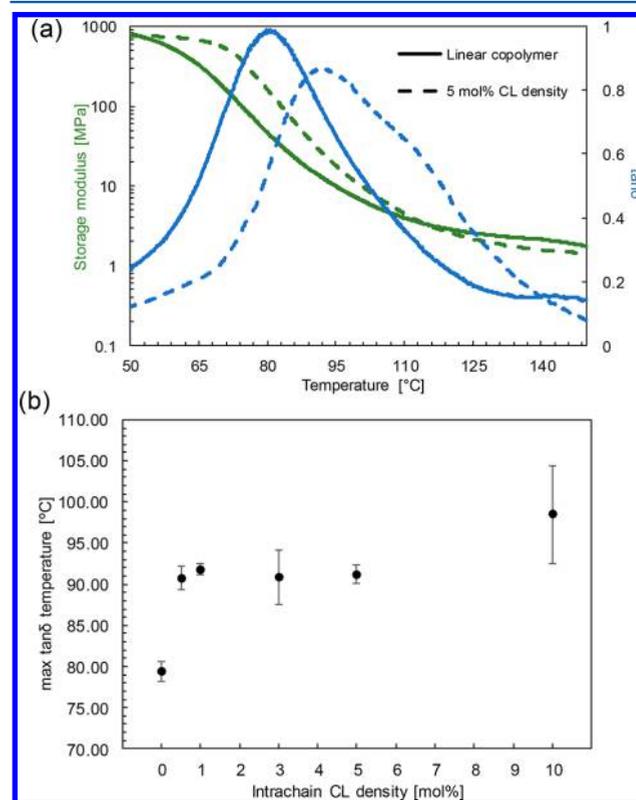

Figure 3. DMA curves of linear copolymer and 5 mol % intrachain CL density (a). Change in maximum tan δ temperature as a function of intrachain cross-link density (b). Average values from 3 to 5 measurements and their standard divisions are shown.

reached a rubbery region, and was stopped before the melting point. An initial temperature of 50 °C was chosen to facilitate the measurements of samples from higher cross-linked chains, which were very brittle. Again, specimens made from the 15 mol % cross-link density polymer failed even at these conditions, and therefore not enough reliable data were collected.

It can be seen that the storage modulus behavior is somewhat different between the linear and 5 mol % cross-link density polymers. Decline in storage modulus starts at 50−70 °C for the linear copolymer, while the samples made from intrachain cross-linked polymers remain constant. Decrease in storage modulus for these samples start only above 70 °C. At 50 °C the linear polymer already begins to "soften" while the intrachain cross-linked polymers are still glassy. This behavior is an indication of the glass transition to the rubbery region difference between the linear and 5 mol % cross-linked polymers which is better expressed by the maximum of tan δ. For example, in Figure 3a, the linear copolymer presents this transition at 79.43 ± 1.22 °C compared to 91.18 ± 1.16 °C for the 5 mol % cross-link density polymer. This observation indicates that intramolecular cross-linking can be beneficial in maintaining mechanical properties at higher temperatures.

As temperature increases and force is applied to induce movement of the chains, these cross-links increase the intramolecular friction, requiring additional energy to achieve mobility; i.e., higher temperatures are needed in order to reach the rubbery region. Figure 3b summarizes the maximum tan δ temperature for all samples studied. The glass transition temperature increases as a function of cross-link density, from 79.43 $\pm$ 1.22 °C for the linear copolymer and up to 98.50 $\pm$ 5.92 °C for the 10 mol % intrachain cross-link density. Intramolecular chain collapse increases the density of organic matter, reducing the "empty" space among polymer chains, and therefore chain mobility and free volume are reduced, explaining the increase in T_g.

Differential Scanning Calorimetry. While previous DSC studies have shown that intramolecular cross-linking increases the glass transition temperature,[13,31,32] we repeated these measurements to support the results seen in DMA (Figure 4). Measurements were carried out at 10 °C min^{-1} from room
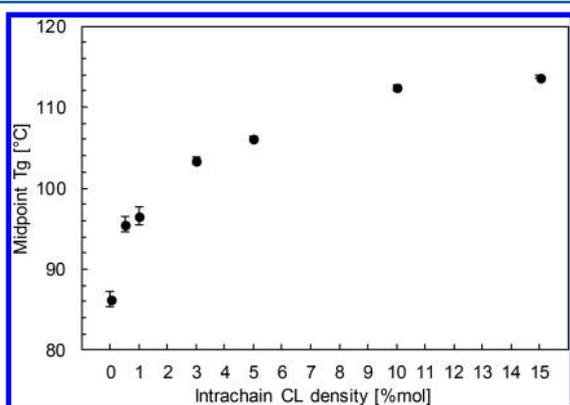
Figure 4. Change in T_g (DSC) as a function of intramolecular cross-link density. Average values from three measurements and their standard divisions are shown.

temperature to 200 °C. Reported glass transitions are from the second heating sequence. The linear copolymer presented a T_g of 86.29 $\pm$ 0.88 °C, whereas an atactic homopolymer of PMMA has a T_g of 125 °C.[33] This reduction is expected because inclusion of AEMA into PMMA has previously been shown to reduce the T_g.[34] As intramolecular cross-link density increases, the T_g rises up to 113.74 $\pm$ 0.18 °C. A measurement for the 15 mol % cross-link density polymer was possible to obtain due to the fact that for DSC measurements a powder is needed, in contrast to tensile tests and DMA measurements. The trends observed in DMA are clearly confirmed by DSC, with a monotonic increase in T_g as a function of cross-link density observed. Table 2 summarizes all the measured properties for

the materials made from SCPNs with different cross-link densities but the same DP as well as the linear polymer precursor.

■ CONCLUSION

We have cast bulk samples made from assemblies of polymer chains with similar DPs but containing different ratios of intramolecular cross-links. Contrary to thermosets that contain intermolecular cross-links, the material obtained is thermoplastic and can be easily dissolved and solvent cast to different shapes. Similar to thermosets, below T_g the elastic modulus was not affected by cross-linking, since the chains are "frozen" and only the chemistry of the chain, not its architecture, affects the elastic properties of the bulk material. However, as the material begins to deform and reaches the plastic region, intramolecular cross-links play a role, leading to a change in parameters such as peak stress and toughness. In addition, thermomechanical properties are also significantly affected by these intramolecular cross-links. Even a slight amount of covalent intramolecular chain collapse affects the motion of the polymer. At high cross-link densities, the polymer chains resemble organic nanoparticles with low entanglements, in which the thermal motion is more restricted than the motion of a linear chain.

■ ASSOCIATED CONTENT

⑤ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.7b01472.

Figures S1−S37 (PDF)

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: charles@technion.ac.il (C.E.D.).
*E-mail: ms2682@cornell.edu (M.N.S.).

ORCID ⑩
Feng Wang: 0000-0003-0524-8729
Charles E. Diesendruck: 0000-0001-5576-1366

Notes
The authors declare no competing financial interest.

Table 2. Mechanical and Thermomechanical Characterization of P(MMA-co-AEMA) at Different Intrachain Cross-Link Density

cross-link density [mol %][a]	elastic modulus [GPa][a]	peak stress [MPa][a]	toughness [MPa][a]	max tan δ temp [°C][b]	T_g from DSC [°C][c]
0	1.61 $\pm$ 0.12	32.39 $\pm$ 1.85	0.86 $\pm$ 0.19	79.43 $\pm$ 1.22	86.29 $\pm$ 0.88
0.5	1.61 $\pm$ 0.17	25.49 $\pm$ 0.61	0.92 $\pm$ 0.23	90.71 $\pm$ 1.43	95.56 $\pm$ 0.94
1	1.79 $\pm$ 0.06	24.63 $\pm$ 0.70	0.59 $\pm$ 0.10	91.80 $\pm$ 0.72	96.59 $\pm$ 1.16
3	1.65 $\pm$ 0.18	19.86 $\pm$ 0.95	0.22 $\pm$ 0.05	90.86 $\pm$ 3.33	103.43 $\pm$ 0.39
5	1.41 $\pm$ 0.22	20.55 $\pm$ 2.46	0.29 $\pm$ 0.07	91.18 $\pm$ 1.16	106.21 $\pm$ 0.13
10	1.47 $\pm$ 0.21	23.29 $\pm$ 0.83	0.34 $\pm$ 0.05	98.50 $\pm$ 5.92	112.45 $\pm$ 0.35
15	-	-	-	-	113.74 $\pm$ 0.18

[a]Calculated from stress−strain curves. [b]Received from DMA. [c]Received from DSC.

■ REFERENCES

(1) Bower, D. I. *An Introduction to Polymer Physics*; Cambridge University Press: 2002.

(2) Steinhauser, M. O. A molecular dynamics study on universal properties of polymer chains in different solvent qualities. Part I. A review of linear chain properties. *J. Chem. Phys.* **2005**, *122* (9), 094901.

(3) Gao, C.; Yan, D. Hyperbranched polymers: from synthesis to applications. *Prog. Polym. Sci.* **2004**, *29* (3), 183−275.

(4) Mavila, S.; Eivgi, O.; Berkovich, I.; Lemcoff, N. G. Intramolecular cross-linking methodologies for the synthesis of polymer nanoparticles. *Chem. Rev.* **2016**, *116* (3), 878−961.

(5) Kuhn, V.; Majer, H. Die selbstvernetzung von fadenmolekülen. *Makromol. Chem.* **1956**, *18* (1), 239−253.

(6) Kuhn, W.; Balmer, G. Crosslinking of single linear macromolecules. *J. Polym. Sci.* **1962**, *57* (165), 311−319.

(7) Allen, G.; Burgess, J.; Edwards, S.; Walsh, D. In On the Dimensions of Intramolecularly Crosslinked Polymer Molecules. I. The Synthesis and Chemical Characterization of Intramolecularly Crosslinked Polystyrene Molecules Having a Narrow Distribution of Molecular Weight, *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*; The Royal Society: 1973; pp 453−463.

(8) Tsyurupa, M.; Mrachkovskaya, T.; Maslova, L.; Timofeeva, G.; Dubrovina, L.; Titova, E.; Davankov, V.; Menshov, V. Soluble intramolecularly hypercrosslinked polystyrene. *React. Polym.* **1993**, *19* (1−2), 55−66.

(9) Martin, J. E.; Eichinger, B. Dimensions of intramolecularly crosslinked polymers. 1. Theory. *Macromolecules* **1983**, *16* (8), 1345−1350.

(10) Mecerreyes, D.; Lee, V.; Hawker, C. J.; Hedrick, J. L.; Wursch, A.; Volksen, W.; Magbitang, T.; Huang, E.; Miller, R. D. A Novel Approach to Functionalized Nanoparticles: Self-Crosslinking of Macromolecules in Ultradilute Solution. *Adv. Mater.* **2001**, *13* (3), 204−208.

(11) Elsabahy, M.; Wooley, K. L. Strategies toward well-defined polymer nanoparticles inspired by nature: Chemistry versus versatility. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50* (10), 1869−1880.

(12) Lemcoff, N. G.; Spurlin, T. A.; Gewirth, A. A.; Zimmerman, S. C.; Beil, J. B.; Elmer, S. L.; Vandeveer, H. G. Organic nanoparticles whose size and rigidity are finely tuned by cross-linking the end groups of dendrimers. *J. Am. Chem. Soc.* **2004**, *126* (37), 11420−11421.

(13) Cherian, A. E.; Sun, F. C.; Sheiko, S. S.; Coates, G. W. Formation of nanoparticles by intramolecular cross-linking: following the reaction progress of single polymer chains by atomic force microscopy. *J. Am. Chem. Soc.* **2007**, *129* (37), 11350−11351.

(14) Beck, J. B.; Killops, K. L.; Kang, T.; Sivanandan, K.; Bayles, A.; Mackay, M. E.; Wooley, K. L.; Hawker, C. J. Facile preparation of nanoparticles by intramolecular cross-linking of isocyanate functionalized copolymers. *Macromolecules* **2009**, *42* (15), 5629−5635.

(15) Harth, E.; Horn, B. V.; Lee, V. Y.; Germack, D. S.; Gonzales, C. P.; Miller, R. D.; Hawker, C. J. A facile approach to architecturally defined nanoparticles via intramolecular chain collapse. *J. Am. Chem. Soc.* **2002**, *124* (29), 8653−8660.

(16) He, J.; Tremblay, L.; Lacelle, S.; Zhao, Y. Preparation of polymer single chain nanoparticles using intramolecular photodimerization of coumarin. *Soft Matter* **2011**, *7* (6), 2380−2386.

(17) Murray, B. S.; Fulton, D. A. Dynamic covalent single-chain polymer nanoparticles. *Macromolecules* **2011**, *44* (18), 7242−7252.

(18) Tuten, B. T.; Chao, D.; Lyon, C. K.; Berda, E. B. Single-chain polymer nanoparticles via reversible disulfide bridges. *Polym. Chem.* **2012**, *3* (11), 3068−3071.

(19) Mavila, S.; Diesendruck, C. E.; Linde, S.; Amir, L.; Shikler, R.; Lemcoff, N. G. Polycyclooctadiene complexes of rhodium (I): direct access to organometallic nanoparticles. *Angew. Chem., Int. Ed.* **2013**, *52* (22), 5767−5770.

(20) Bae, S.; Galant, O.; Diesendruck, C. E.; Silberstein, M. N. Tailoring single chain polymer nanoparticle thermomechanical behavior by cross-link density. *Soft Matter* **2017**, *13* (15), 2808−2816.

(21) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J.; Hirschberg, J. K.; Lange, R. F.; Lowe, J. K.; Meijer, E. Reversible polymers formed from self-complementary monomers using quadruple hydrogen bonding. *Science* **1997**, *278* (5343), 1601−1604.

(22) Schmidt, G.; Malwitz, M. M. Properties of polymer−nanoparticle composites. *Curr. Opin. Colloid Interface Sci.* **2003**, *8* (1), 103−108.

(23) Mackay, M. E.; Dao, T. T.; Tuteja, A.; Ho, D. L.; Van Horn, B.; Kim, H.-C.; Hawker, C. J. Nanoscale effects leading to non-Einstein-like decrease in viscosity. *Nat. Mater.* **2003**, *2* (11), 762−766.

(24) Balazs, A. C.; Emrick, T.; Russell, T. P. Nanoparticle polymer composites: where two small worlds meet. *Science* **2006**, *314* (5802), 1107−1110.

(25) Jeon, I.-Y.; Baek, J.-B. Nanocomposites derived from polymers and inorganic nanoparticles. *Materials* **2010**, *3* (6), 3654−3674.

(26) Levy, A.; Wang, F.; Lang, A.; Galant, O.; Diesendruck, C. E. Intramolecular Cross-Linking: Addressing Mechanochemistry with a Bioinspired Approach. *Angew. Chem.* **2017**, *129*, 6531−6534.

(27) Sanchez-Sanchez, A.; Akbari, S.; Etxeberria, A.; Arbe, A.; Gasser, U.; Moreno, A. J.; Colmenero, J.; Pomposo, J. A. Michael" nanocarriers mimicking transient-binding disordered proteins. *ACS Macro Lett.* **2013**, *2* (6), 491−495.

(28) Chiefari, J.; Chong, Y.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P.; Mayadunne, R. T.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Living free-radical polymerization by reversible addition−fragmentation chain transfer: the RAFT process. *Macromolecules* **1998**, *31* (16), 5559−5562.

(29) http://www.mit.edu/~6.777/matprops/pmma.htmhttp://www.mit.edu/~6.777/matprops/pmma.htm; MIT Database (accessed 06.07.2017).

(30) Gomes, A.; Timbó, A. Influence of crosslinking on the moduli and impact strength of methacrylate polymers. *Polym. Eng. Sci.* **1981**, *21* (12), 745−747.

(31) Wang, F.; Pu, H.; Jin, M.; Wan, D. Supramolecular Nanoparticles via Single-Chain Folding Driven by Ferrous Ions. *Macromol. Rapid Commun.* **2016**, *37*, 330−336.

(32) Cengiz, H.; Aydogan, B.; Ates, S.; Acikalin, E.; Yagci, Y. Intramolecular cross-linking of polymers using difunctional acetylenes via click chemistry. *Des. Monomers Polym.* **2011**, *14* (1), 69−78.

(33) http://polymerdatabase.com/polymer%20classes/Polymethacrylate%20type.html; Polymer Database (accessed 06.07.2017).

(34) Zoller, A.; Kockler, K. B.; Rollet, M.; Lefay, C.; Gigmes, D.; Barner-Kowollik, C.; Guillaneuf, Y. A complete kinetic study of a versatile functional monomer: acetoacetoxyethyl methacrylate (AAEMA). *Polym. Chem.* **2016**, *7* (35), 5518−5525.