

Recyclable Polymers with Boronic-Ester Dynamic Bonds Prepared by Miniemulsion Polymerization

Saeid Tajbakhsh¹, Faezeh Hajiali¹, Milan Marić^{1}*

¹Department of Chemical Engineering, McGill University, 3610 University St. Montreal, H3A 0C5 Quebec, Canada.

KEYWORDS

Methacrylates, dynamic cross-linking, miniemulsion, recyclability, nitroxide mediated polymerization.

ABSTRACT

Polymers with boronic ester dynamic covalent bonds were synthesized by nitroxide-mediated miniemulsion polymerization of isobornyl methacrylate (IBOMA, 71% bio-content), alkyl methacrylates (average aliphatic size of 13.0, C13MA, 76% bio-content), glycerol monomethacrylate (GMMA) and 4-vinylphenylboronic acid (VPBA). The miniemulsion polymerization of all monomers was enabled by the esterification reaction between GMMA and VPBA and the synthesis of (VPBA+GMMA) dimer prior to the polymerization. The formation of boronic ester dynamic covalent bonds was confirmed by rheological and mechanical

measurements, indicating a higher stiffness by increasing the dimer content from 5 to 15% in the initial feed. Cross-linked polymers showed high reprocessing capability with comparatively simple recycling process (at 80 °C for 45 minutes) and the high organic solvent absorbance of polymers (swelling ratio up to 153%). Furthermore, it was shown that the addition of VPBA and GMMA significantly improved the heat resistance of polymers up to 121 °C, compared to the IBOMA/C13MA copolymers (without GMMA and VPBA functional monomers).

INTRODUCTION

Preparation of polymers containing boronic ester dynamic covalent bonds has been of interest due to their exceptional recyclability and self-healing properties¹⁻³. These materials have been widely used for the preparation of hydrogels and related polymer resins for applications such as tissue engineering and drug delivery^{3, 4}, optical devices⁵, solid polymer electrolytes (SPEs)⁶ and coatings⁷. Different methods were utilized to produce polymers with boronic ester cross-linking bonds^{2, 8}. One of the most common methods is the synthesis of diol-functionalized polymer and boronic acid-containing polymers separately and mixing them together^{9, 10}. The synthesis of each polymer resin or the mixing process generally involves using organic solvents, which intensifies the environmental and health concerns associated with the process^{11, 12}. Although using water as the dispersant phase in the system seems beneficial, the synthesis of materials containing boronic ester bonds in a water-based system has always been problematic due to relatively high water-solubility of monomers containing the boronic acid or diol functional groups¹³⁻¹⁵. Furthermore, the copolymerization of these monomers with water-insoluble monomers in water-based or emulsion systems usually results in uncontrolled formation of hydrogels with broad molecular weight distribution and low monomer conversion^{3, 16}. We prepared polymers containing boronic ester

dynamic cross-linking bonds in an organic solvent (toluene) previously where we attempted to use commercially available monomers with high bio-content¹⁷. This was done presumably to decrease the carbon footprint of the process while still getting the desirable properties incorporated into the polymer. We attempted to take our process one step farther and eliminate the use of organic solvent in the synthesis of the recyclable polymers with boronic ester dynamic cross-links by adopting controlled radical polymerization in miniemulsion. To enhance the environmental sustainability of the polymers, 85-95 molar% of polymer resins were made of partially bio-based methacrylic monomers. Isobornyl methacrylate (IBOMA, 71% bio carbon content) derived from pine sap (camphene) has a high glass transition temperature (T_g) ($T_{g,P(IBOMA)} = 110\sim 200\text{ }^{\circ}\text{C}$)^{18, 19} and used to improve the T_g of polymers²⁰. Alkyl methacrylates with average side-chain aliphatic size of 13.0 (termed here as C13MA, 76% bio carbon content, derived from natural oils) was incorporated into resins to decrease the T_g ($T_{g,P(C13MA)} = -46\text{ }^{\circ}\text{C}$)¹⁸ and improve the flexibility of polymer chains^{21, 22}. Using IBOMA and C13MA, polymers with tunable T_g can be produced to meet the criteria for a specific application²²⁻²⁵. Nitroxide mediated polymerization (NMP) as one of the simplest reversible deactivation radical polymerization (RDRP) techniques was utilized to improve control over the polymerization (linear increase of average molecular weight (M_n) versus monomer conversion (X)), to reduce discoloration, to obtain tighter molecular weight distribution (D) leading to lower viscosities for application in coatings and to enhance chain-to-chain compositional homogeneity and the formation of well-defined microstructures²⁶⁻²⁹. For the nitroxide, we used 3-(((2-cyanopropan-2-yl)oxy)-(cyclohexyl)amino)-2,2-dimethyl-3-phenylpropanenitrile (Dispolreg 007) alkoxyamine to initiate the miniemulsion polymerization of methacrylates, without any controlling co-monomer as was typically required for NMP, at temperatures below $100\text{ }^{\circ}\text{C}$ ^{30, 31}.

For miniemulsion, all that was needed besides the monomers and nitroxide was surfactant and long chain alkyl-containing co-stabilizers³²⁻³⁴.

The incorporation of boronic ester bonds was more challenging; it required the esterification of glycerol monomethacrylate (GMMA, 2,3-dihydroxypropyl methacrylate) and 4-vinylphenylboronic acid (VPBA) as monomers incorporated into the respective polymer chains. Different methods have been applied for the RDRP of GMMA or VPBA (separately)^{13, 35-38}. Chen et al¹⁴ prepared homopolymers of unprotected VPBA (PVPBA) (M_n up to 16.2 kg mol⁻¹ and $\bar{D}$ <1.21) by RAFT polymerization in DMF solvent. Jesson et al³⁹ synthesized homopolymers of GMMA (PGMMA) with relatively high M_n (M_n up to 159.5 kg mol⁻¹ and $\bar{D}$ <1.32) by RAFT emulsion polymerization of isopropylideneglycerol methacrylate with PGMMA-based macroinitiator followed by the subsequent removal of acetal protecting groups in acidic solution. However, we are unaware of reports concerning the successful controlled polymerization for the preparation of boronic ester containing materials in miniemulsion. The VPBA-containing or GMMA-containing polymer latexes cannot be produced separately as the VPBA and GMMA are water-soluble and cannot be effectively available inside the monomer droplets during the miniemulsion polymerization^{13, 15}. We report an approach using a pre-prepared dimer with the boronic acid/diol ester, which was subsequently added to the hydrophobic monomer mixture. After polymerization, the boronic ester can be de-activated, resulting in the respectively functionalized chains. Addition of water further allowed the esterification to be repeated, thus providing a moisture-controlled dynamic cross-linking process.

RESULTS AND DISCUSSION

Preparation of VPBA + GMMA dimer

For a successful miniemulsion polymerization, the monomers should be stabilized within the nanometer-sized micelles. Typically, a combination of surfactant and co-stabilizer is required to afford the proper colloidal stability²⁸. However, the monomers should exhibit sufficient hydrophobicity to exclusively have polymerization occur inside the stabilized particles (the requisite for miniemulsion polymerization). IBOMA and C13MA monomers are highly hydrophobic, which makes them readily available inside the monomer latex droplets²². However, the GMMA and VPBA are water-soluble and thus limits their availability for polymerization inside the monomer droplets^{40, 41}. We attempted to adopt miniemulsion polymerization containing these monomers by synthesizing a dimer of GMMA and VPBA monomers (termed simply as BG dimer going forward) beforehand to increase their hydrophobicity and use them in miniemulsion NMP. The BG dimer has the boronic ester bond within its structure and is theoretically able to degrade into the GMMA and VPBA in the presence of water. The FTIR spectrum of VPBA and GMMA monomers and the synthesized BG dimer are depicted in Figure S1 (Supporting Information). The successful formation of BG dimer has been previously proven in the literature^{2, 8}. The peaks at a wavenumber of 3350-3500 cm^{-1} correspond to O-H stretching in molecules. The change in the O-H peak position in IR spectrum is due to the different O-H bonds in the monomer structures. Boronic acid groups contain B-O-H bonds, while GMMA has 2 C-O-H groups. This slightly changes the position of peak for OH stretches. A considerable decrease in O-H stretch was observed after the successful formation of BG dimer monomer. This confirms the formation of boronic ester bonds between VPBA and GMMA monomers².

Next, the miniemulsion NMP of IBOMA/C13MA/BG dimer was conducted at 90 °C in the presence of Dispolreg 007 alkoxyamine. Using Dispolreg 007 alkoxyamine, no controlling comonomer is required for nitroxide mediated polymerization of methacrylates^{30, 42}. A target

number average molecular weight ($M_{n,target}$) of 45 kg mol^{-1} was considered for all the miniemulsion NMPs. This $M_{n,target}$ was chosen to show the possibility of making relatively long polymer chains in miniemulsion using this method, to incorporate multiple BG dimers into the chains and to produce IBOMA/C13MA/BG dimer polymers with similar chain length to our previous studies concerning IBOMA/C13MA statistical copolymers prepared in miniemulsion²². Based on our previous study, a lower incorporation of vinylic head of BG dimer into the polymer chains is expected compared to the methacrylic group¹⁷. This probably results in incomplete incorporation of some BG dimers into the polymer chains. A schematic miniemulsion polymerization of the monomers is presented in Figure 1. Three different initial molar concentrations of BG dimer were used in the miniemulsion polymerizations (Table 1) to study the effect of dimer concentration on the polymerization kinetics, cross-linking density and eventually mechanical and chemical properties of final polymers. As shown in Figure 2 (a) and (b) and Table 1, a high final dispersity ($\bar{D}$) for polymer chains was observed for all the experiments in miniemulsion, although a linear increase of $\ln((1-X)^{-1})$ plots (X = monomer conversion) and M_{ns} with X was generally witnessed. The relatively high $\bar{D}$ was expected as the dimer creates cross-linking bonds between the polymer chains and prevents the polymerization from proceeding to higher conversions. For Dimer 15%, $\bar{D} = 5.0$ was observed, indicating the formation of boronic ester bonds between polymer chains at higher conversions. However, relatively fast polymerization ($t_{\text{reaction}} < 210 \text{ min}$), polymers with high M_{ns} and latexes without coagulation or precipitation resulted for all polymerizations. Our previous study on the miniemulsion polymerization of IBOMA/C13MA in a similar system (same surfactant and co-stabilizer with the same concentration) indicated zeta-potentials between -38 to -43 mV²⁵. This suggests the possibility of a high colloidal stability for the polymer latexes. The M_n versus conversion (X) plot was linear for all miniemulsion polymerizations with higher M_{ns}

than the predicted linear relationship (Figure 2 (b)). The deviation from the theoretical line is partly due to the slow initiation of Dispolreg 007 alkoxyamine at the beginning of the polymerization, which results in higher M_n at different conversions⁴³. Furthermore, the calibration against PMMA standards without applying the Mark-Houwink-Sakurada coefficients for IBOMA/C13MA/GMMA/VPBA homopolymers can cause a slight over-prediction⁴⁴. The parallel increase of the slope of M_n versus X with theoretical line is probably due to the boronic ester cross-linking, which limits the polymer chain growth. Figure 2 (c) displays the particle size during the course of polymerizations. The final particle size and the final particle size distribution are presented in Table 1 and Figure 2, respectively. The particle size distributions (Figure 2 (d)) show a small population of micrometer-sized particles, suggesting some coagulation and formation of cross-linked latex particles.

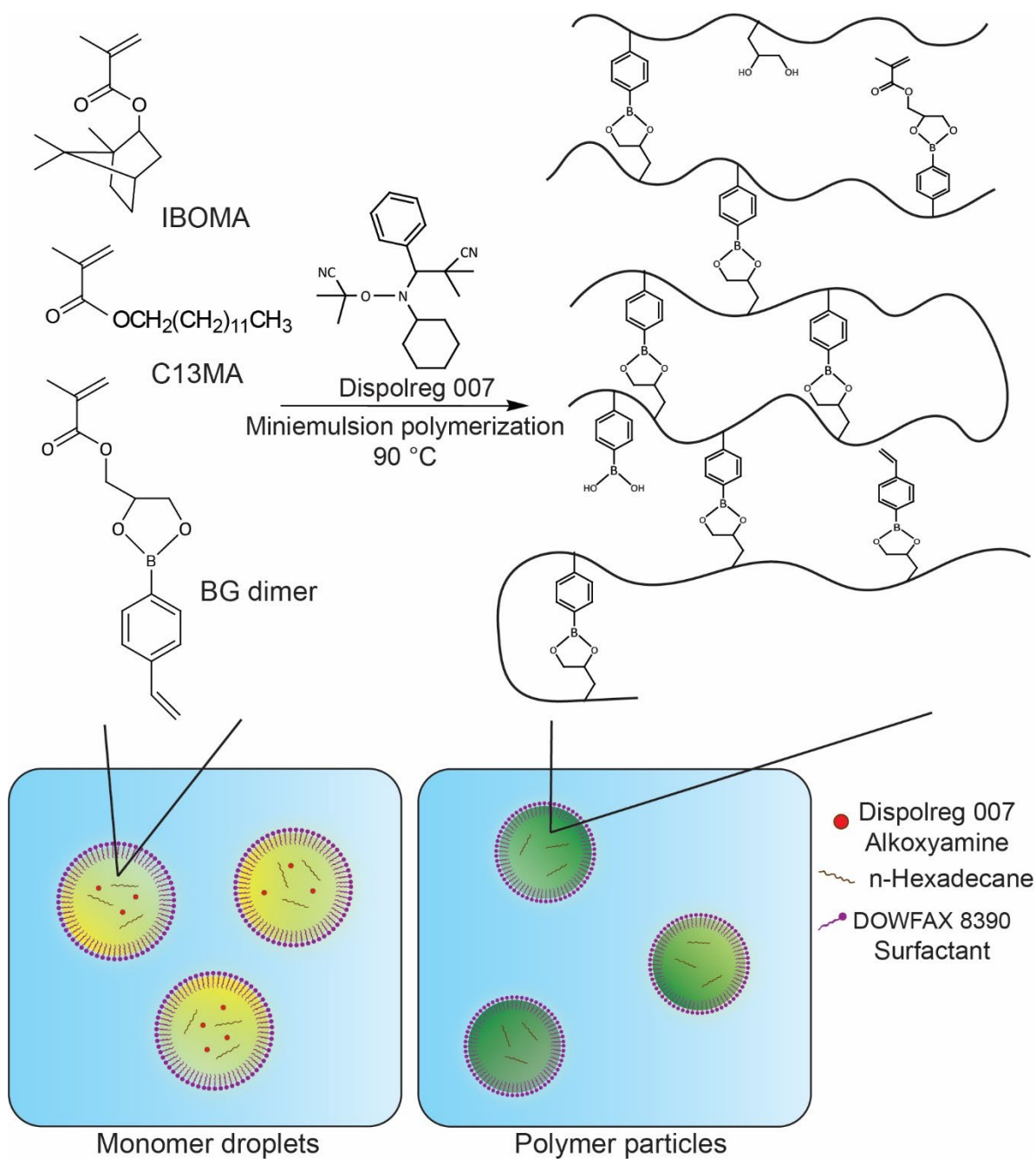


Figure 1. Scheme of procedure for preparation of water-borne polymers with intrinsic dynamic crosslinking bonds.

Table 1. Summary of experiments for nitroxide-mediated miniemulsion polymerization of IBOMA/C13MA monomers and BG dimer using Dispolreg 007 initiator.

Experiment ID	Initial monomer % ^b (Dimer/IBOMA/C13MA)	Reaction time (min)	$M_{n,final}$ ^c (kg mol ⁻¹)	X ^c (%)	$\bar{D}$ ^c	[IBOMA] ₀ ^d (M)	[C13MA] ₀ (M)	[BG Dimer] ₀ (M)	[Dispolreg 007] (M)	Particle size (nm) ^e	PDI
Dimer 5% ^a	5/30/65	210	40.6	78.1	1.9	0.282	0.610	0.047	0.005	297	0.269
Dimer 10%	10/30/60	150	37.8	47.5	1.8	0.285	0.570	0.095	0.005	294	0.204
Dimer 15%	15/25/60	210	48.8	64.6	5.0	0.239	0.573	0.143	0.005	280	0.197

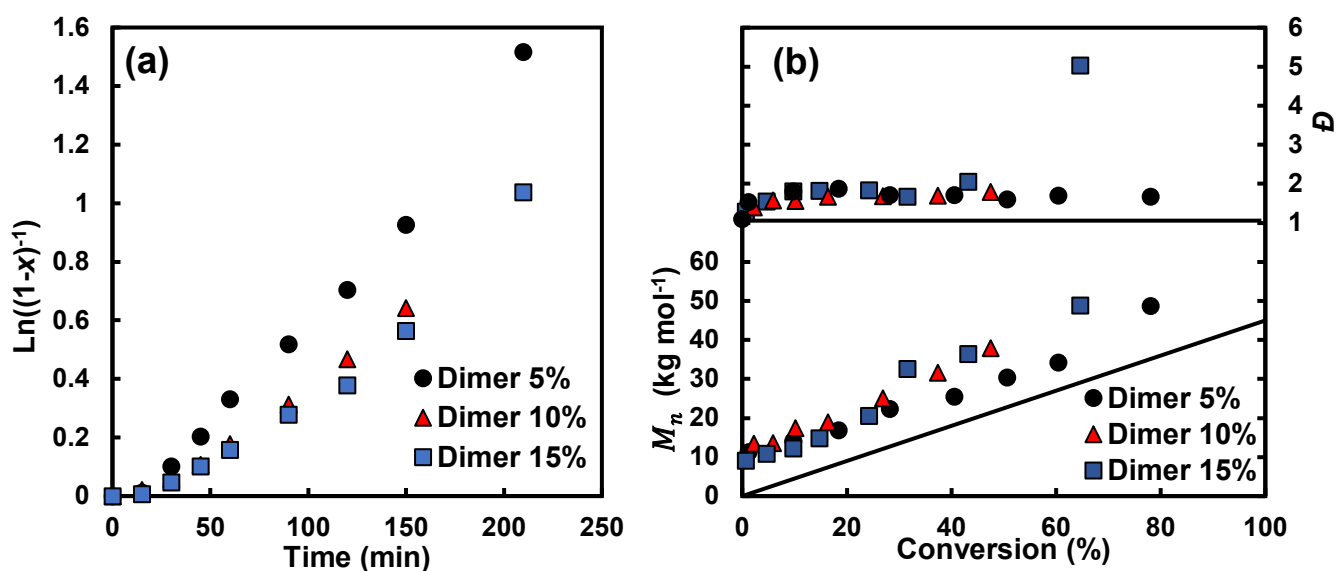
^a Nitroxide mediated miniemulsion polymerization of monomers with 5 mol% BG dimer in the initial feed composition at 90 °C. The monomer content for all the miniemulsions was 24 wt%. The latexes were stabilized by adding 2 wt% Dowfax™ 8390 and 0.8 wt% n-hexadecane relative to monomers.

^b The mol % of each monomer in initial monomer mixture.

^c The final number-average molecular weight (M_n), overall monomer conversion (X) and dispersity ($\bar{D}$) were measured by GPC with PMMA standards in THF at 40 °C. The target number-average molecular weight $M_{n,target}$ for all the miniemulsion polymerizations was 45 kg mol⁻¹. The monomer conversion (X) was estimated by comparing the relative peak areas of polymer and monomers.

^d The initial concentration of IBOMA monomer in the miniemulsion.

^e The final Z-average particle size reported from DLS.



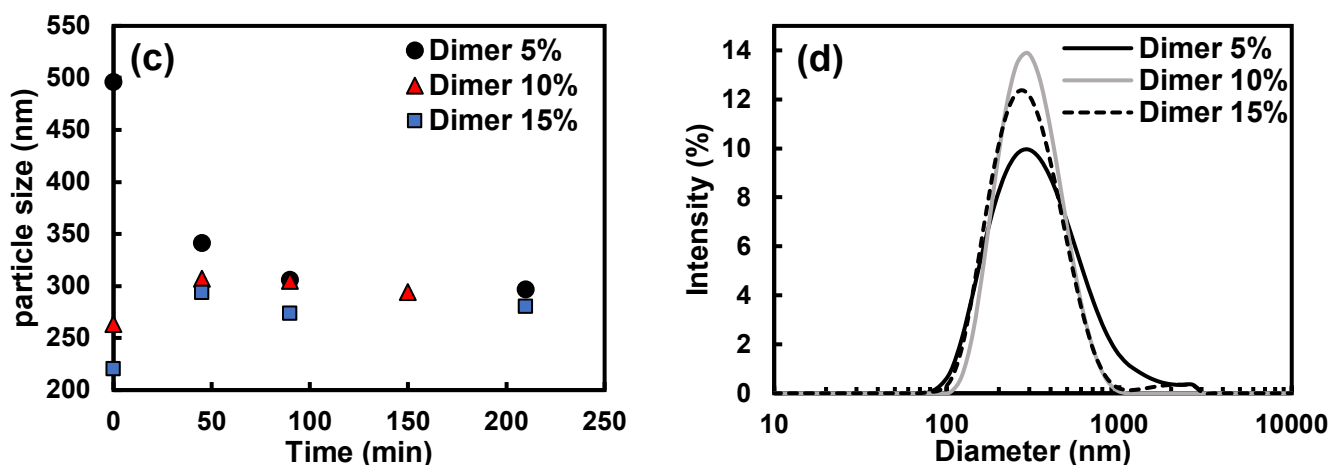


Figure 2. The miniemulsion polymerization of different ratios of BG dimer/IBOMA/C13MA using Dispolreg 007 initiator at 90 °C: (a) semi-logarithmic kinetic plots of $\ln[(1-X)^{-1}]$ (X = monomer conversion) versus reaction time (b) number average molecular weight M_n and dispersity D versus conversion (X) (c) Z-average particle size over reaction time; (d) the final particle size distribution for each experiment. Dimer 5% (black circles, ●); Dimer 10% (red triangles, ▲); Dimer 15% (blue squares, ■).

After the preparation step, the latexes were dried inside a fume hood at ambient temperature. The drying and formation of the polymer film took 24 hours to complete. The final polymer coating was transparent and exhibited a good adhesion to glass (Pyrex™ petri dish). Figure S2 (Supporting Information) demonstrates the polymer latex and film formation for Dimer 15% sample. It was previously shown that polymers containing boronic ester bonds have self-healing properties at room temperature because of the ability of boronic ester groups to change bonds (associative dynamic covalent network) within the polymer structure in presence of water¹⁷. In this study, the network formation probably happened during the film formation process and boronic ester bonds can be formed between polymer chains while the polymers remained relatively flexible due to the relatively low melting point. There was a sufficient concentration of water in the early drying

stages to permit some movement before the polymers eventually stiffened as the water was evaporated.

To check the availability of BG dimer monomers inside the polymer structure, FTIR results of Dimer 5-15% samples were analyzed and compared together (Figure S3 and Figure S4 (Supporting Information)). Peaks at 653 cm^{-1} (CB stretching, HO-B-O and O-B-CC bending) and 1368 cm^{-1} (BO stretching) showed an increase in intensities with increasing the initial BG dimer content from 5 to 15%, exhibiting the availability of BG dimer monomers within the polymer⁴⁵⁻⁴⁷. The peaks at 1611 and 1640 cm^{-1} indicated the C-C stretching for the aliphatic ring in IBOMA and C=C and C-C stretching from the phenyl groups in the dimers. The broad intensity peak at 3446 cm^{-1} corresponded to O-H stretching, which increased with increasing the BG dimer content. Although the samples were dried under vacuum at room temperature before the test, this peak could also be due to the water trapped inside the polymer structure or the existence of un-cross-linked BG dimers (i.e. VPBA and GMMA monomers) within the polymer.

The solid-state ^{11}B NMR spectrum in Figure S5 (Supporting Information) displays ^{11}B chemical shifts at $\delta = 19\text{-}21\text{ ppm}$, indicating the boronic esters and boronic acid groups^{48, 49}. Furthermore, the solid-state ^{13}C NMR on Dimer 5%, 10% and 15% (Figure S6, Supporting Information) showed a wide peak at around $\delta = 111\text{ ppm}$, displaying the presence of unreacted dimers, free boronic acid groups (without esterification) and open rings of boronic ester groups in the polymer structure, which enables the self-healing properties.

To further investigate the formation of dynamic cross-linking bonds within the polymer structure, an oscillatory frequency sweep experiment was conducted on the dried samples from frequencies (ω) $1\text{-}1000\text{ rad s}^{-1}$ at $80\text{ }^{\circ}\text{C}$. As depicted in Figure 3, storage modulus (G') was higher than loss

modulus (G'') for all samples at lower frequencies, indicating the dominance of rubbery behavior⁵⁰. This suggests an elastic gel-like behavior for Dimer 5%-15% polymers at 80 °C. A similar result was previously observed for polymers with gel-like structures that contained boronic ester bonds⁵¹. Furthermore, similar results ($G' > G''$ for frequencies lower than the crossover) were obtained in our previous studies on the polymers with similar compositions^{17, 22}. By increasing the BG dimer content, the G' increased, while preserving the linear trend and constant value up to $\omega \cong 100 \text{ rad s}^{-1}$. For Dimer 5% and 10%, a minimum was observed for G'' , which shows the quasi-solid like properties for these polymers⁵². However, the great difference between G' and G'' for Dimer 5% and Dimer 10%, intensified the rubbery behavior. This trend was not indicated for Dimer 15% as the cross-linking density is high enough to maintain elastic solid behavior for a wide range of frequencies (from 1 to 500 rad s^{-1}). At approximately $\omega \cong 100 \text{ rad s}^{-1}$, G'' increased sharply to reach a transition and the G' started to decrease slowly. A sharp increase in G'' was observed for Dimer 5% and 10%, indicating fast relaxation and energy dissipation from the chains. The crossover ($G' = G''$) occurred at crossover frequencies (ω_c) of 315, 450 and 500 rad s^{-1} for Dimer 5%, 10% and 15%, respectively. At $\omega > \omega_c$, the polymers start behaving like viscous liquids and the $G'' > G'$. The crossover and the transition to the liquid state occurred at lower frequencies for Dimer 5% due to the lower cross-linking density compared to Dimer 10% and Dimer 15%.

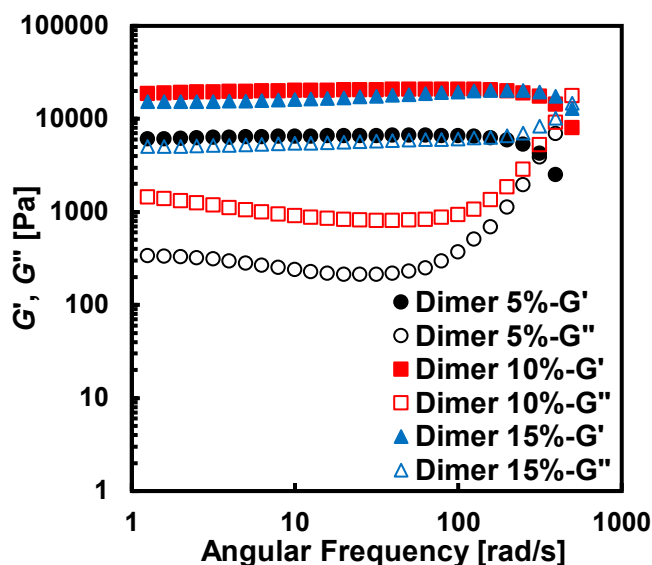
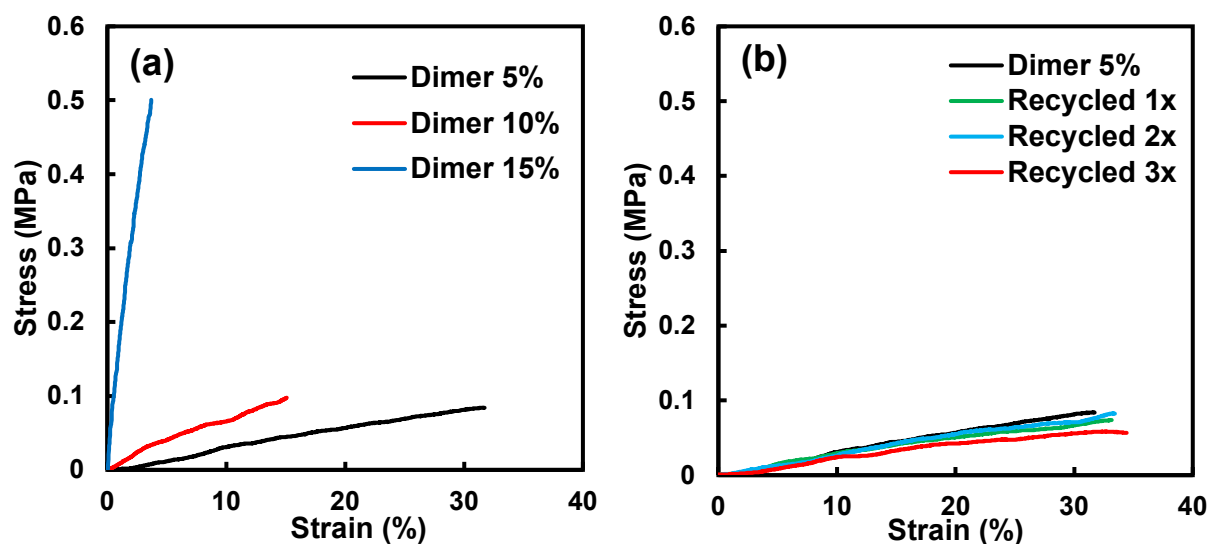


Figure 3. Storage (G') and loss (G'') moduli versus angular frequency under N_2 at 80 °C (1% strain applied). Dimer 5% (black circles); Dimer 10% (red squares); Dimer 15% (blue triangles).

Recyclability of polymers

To check the recyclability of the polymer samples, tensile tests were conducted on samples before and after reprocessing. First, the tensile test was done on the original samples to check the mechanical properties initially (Figure 4 (a)). The Dimer 15% had the highest stress at break, while the elongation was the lowest among the samples (stress and strain at break for Dimer 15% were 0.46 ± 0.06 MPa and 3.6 ± 0.1 %, respectively). Based on the results, increasing the BG dimer concentration in the polymerization feed improved the stress at break and reduced elongation of the samples. This confirms the formation of the dynamic covalent bonds within the polymer structure due to the successful statistical terpolymerization of BG dimer monomers with IBOMA and C13MA. This also indicates the possibility of changing the mechanical properties of the polymer resins by a simple modification of the BG dimer concentration in the initial feed. Next, the reprocessability of the polymers was tested for up to three recycling cycles. The stress and strain at break for all the recycled samples remained in the same range as the original samples,

which suggests a minimal change during the reprocessing. However, the slight change in values was observed due to the presence of unreacted monomers within the polymer structure that may change the mechanical properties during the recycling. This variation may become more pronounced with higher concentrations of dimer in the latex. These monomers can react with other monomers or macroradicals at higher temperatures (reprocessing temperature of 80 °C) and modify the mechanical properties of polymer resins. Toughness (area under stress-strain curve) improvement was noticeable for Dimer 10% and 15% compared to Dimer 5%. The enhancement in tensile results is due to the unreacted BG dimer groups that probably react and form new dynamic bonds after the recycling process. This effect was more pronounced for Dimer 15% because it had the highest BG dimer content and consequently more unreacted boronic ester dimer groups. We also hypothesized that the dip in Young's modulus for Dimer 15% in Table S1 to be due to more rigidity with the increase in boronic ester formation and more recycling steps may have helped to improve the mixing and re-formation of the esters. The tensile results for Dimer 5-15% and the recycled samples were listed in Table S1 (Supporting Information).



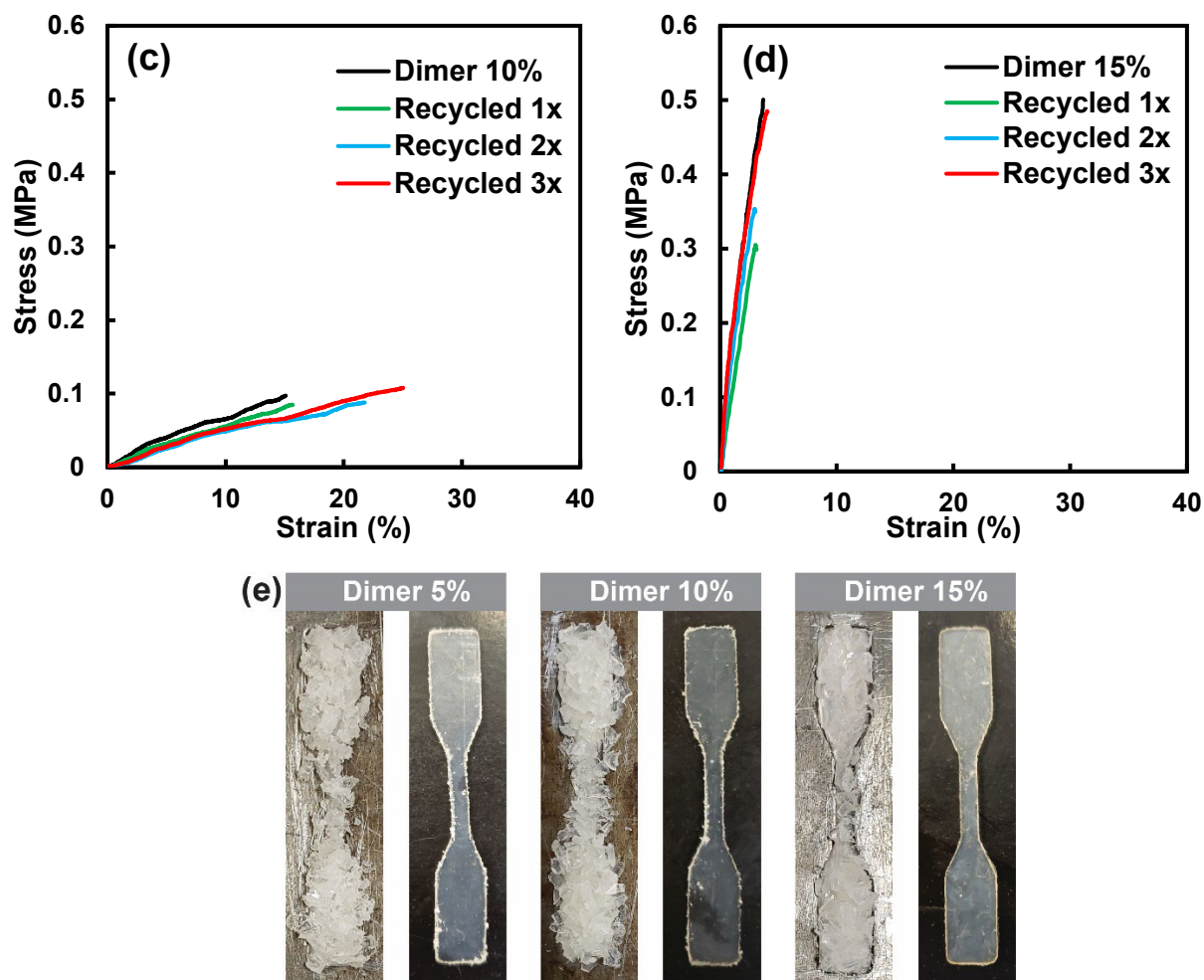
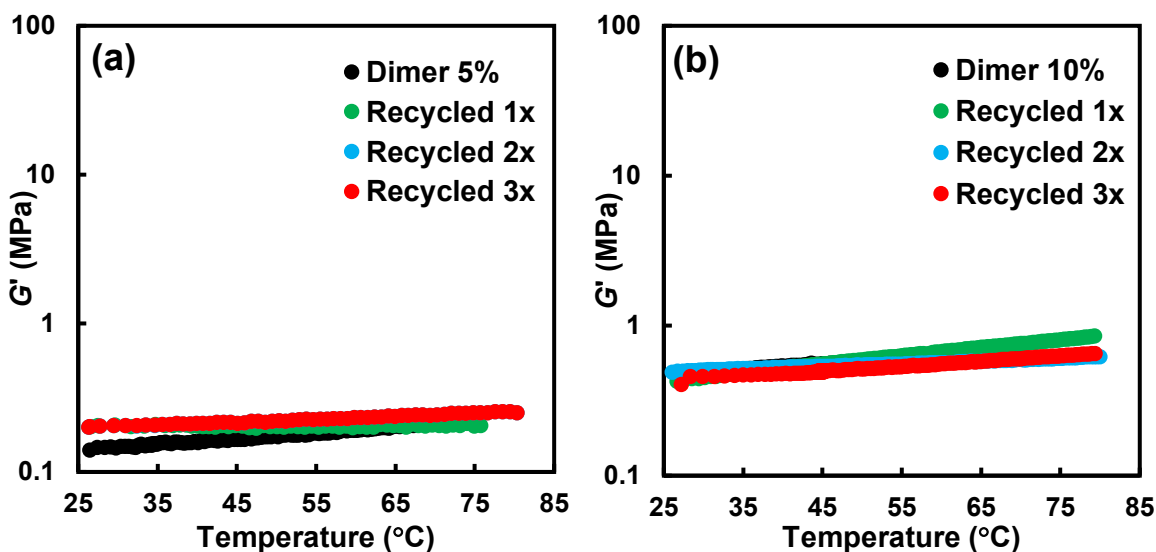


Figure 4. Tensile stress-strain curves for Dimer 5-15% samples before and after recycling. a) tensile results for original samples b) recycling of Dimer 5% sample c) recycling of Dimer 10% sample d) recycling of Dimer 15% sample e) photos of Dimer 5, 10 and 15% samples after recycling process. Grounded samples were hot-pressed at 80 °C for 45 minutes.

To examine the effect of BG dimer concentration on rheological behavior of original and recycled polymers, dynamic mechanical analysis (DMA) (Figure 5) of samples was conducted in the temperature range of 25 to 80 °C. All the samples were in the rubbery state with nearly constant storage modulus during the test. This demonstrates the structural integrity of polymers at higher

temperatures and the availability of dynamic cross-linking within the polymer structure⁸. In addition, the detachment and attachment of boronic ester dynamic bonds obey the associative exchange mechanism, preventing an increase or decrease of storage modulus⁵³. The similarity of storage modulus for original and recycled samples at the rubbery state, suggests a negligible change in cross-linking density and polymer structure during the recycling^{54, 55}. The higher concentration of boronic ester bonds improved the cross-linking density and resulted in the reduced mobility of polymer chains. Therefore, Dimer 15% samples exhibited the highest G' in comparison with Dimer 5% and 10% samples ($G'_{\text{Dimer 15\%}} = 5\text{-}7\text{ MPa}$, $G'_{\text{Dimer 10\%}} = 0.5\text{-}0.8\text{ MPa}$ and $G'_{\text{Dimer 5\%}} = 0.1\text{-}0.3\text{ MPa}$). According to the results, enhancing the boronic ester content of polymers can significantly improve the storage modulus. As an example, increasing the BG dimer concentration from 10 to 15 mol% in initial feed, improved the G' by up to 1400%. This indicates the importance of BG dimer content for modifying the rheological properties of polymers.



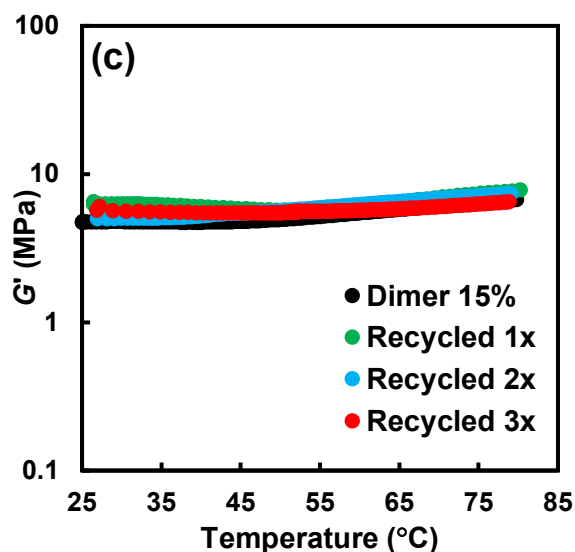


Figure 5. Dynamic mechanical responses for rubbery plateau moduli of samples before and after three recycling stages in the temperature range of 25 to 80 °C. a) Dimer 5% b) Dimer 10% c) Dimer 15%. Original samples before recycling (black circles, ●); first recycle (green circles, ●); second recycle (blue circles, ●); third recycle (red circles, ●).

Swelling test for water-borne samples

The absorption of organic solvents in the water-borne polymer structure was also investigated by measuring the weight change of samples placed in excess toluene. First, the polymers (dried samples) were immersed in toluene for 24 hours. Next, toluene was removed, and samples were completely dried. As a consequence, 53.5 wt%, 56.3 wt% and 63.6 wt% of Dimer 5%, 10% and 15%, respectively, remained insoluble. This shows a high degree of cross-linking bonds within the polymer microstructure. The samples can absorb toluene up to 250% of their original weight in a relatively short time ($t < 300$ minutes). The final swelling ratio (after 24 hours) of samples in toluene were listed in Table S2 (Supporting Information). The results of solvent absorption (for $t < 300$ minutes) were presented in Figure 6 for three water-borne samples. As indicated, Dimer 15% polymer blend had the lowest swelling in toluene due to the comparatively highest cross-

linking density. To examine the possibility of dimer breakage in the presence of toluene, FTIR was conducted on the Dimer 5% sample, submerged in toluene for 24 hours and dried using extra-low lint Kimwipes®. The absence of the broad O-H stretching peak at 3500 cm^{-1} suggested that no dissociation occurred between the VPBA/GMMA boronate ester contained with each dimer (Figure S7, Supporting Information). In addition, the FTIR peaks confirms the existence of a high concentration of toluene in the gel-like structure.

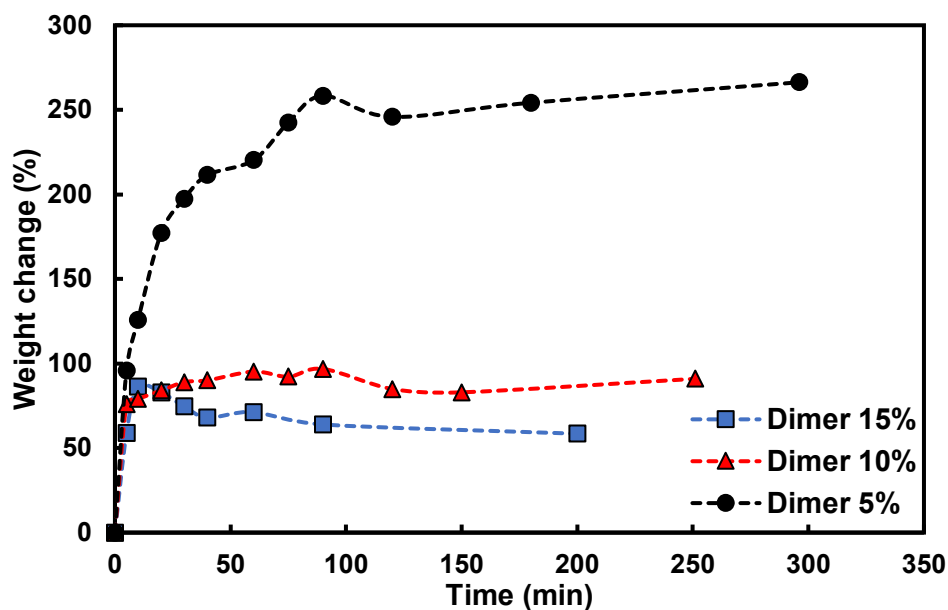


Figure 6. Swelling results for Dimer 5%, 10% and 15% samples in toluene. All the samples absorbed relatively high amount of toluene. Dimer 5% (black circles, ●); Dimer 10% (red triangles, ▲); Dimer 15% (blue squares, ■).

To further study the network stability and possible interactions, water-borne samples were thoroughly submerged in RO water using the same procedure used for the swelling test. No significant weight change was observed in these samples, suggesting the insolubility of samples in water. Due to the low concentration of BG dimers in the polymers and high content of hydrophobic monomers IBOMA and C13MA, the amount of absorbed water is not significant, and

it cannot de-crosslink the whole structure. However, the color of samples slightly changed, and they become cloudy due to the absorbance of water into some of the polymer chains (Figure 7). The FTIR spectrum of samples after submerging them in water for 24 hours (Figure 7) illustrates the presence of some water in the polymer.

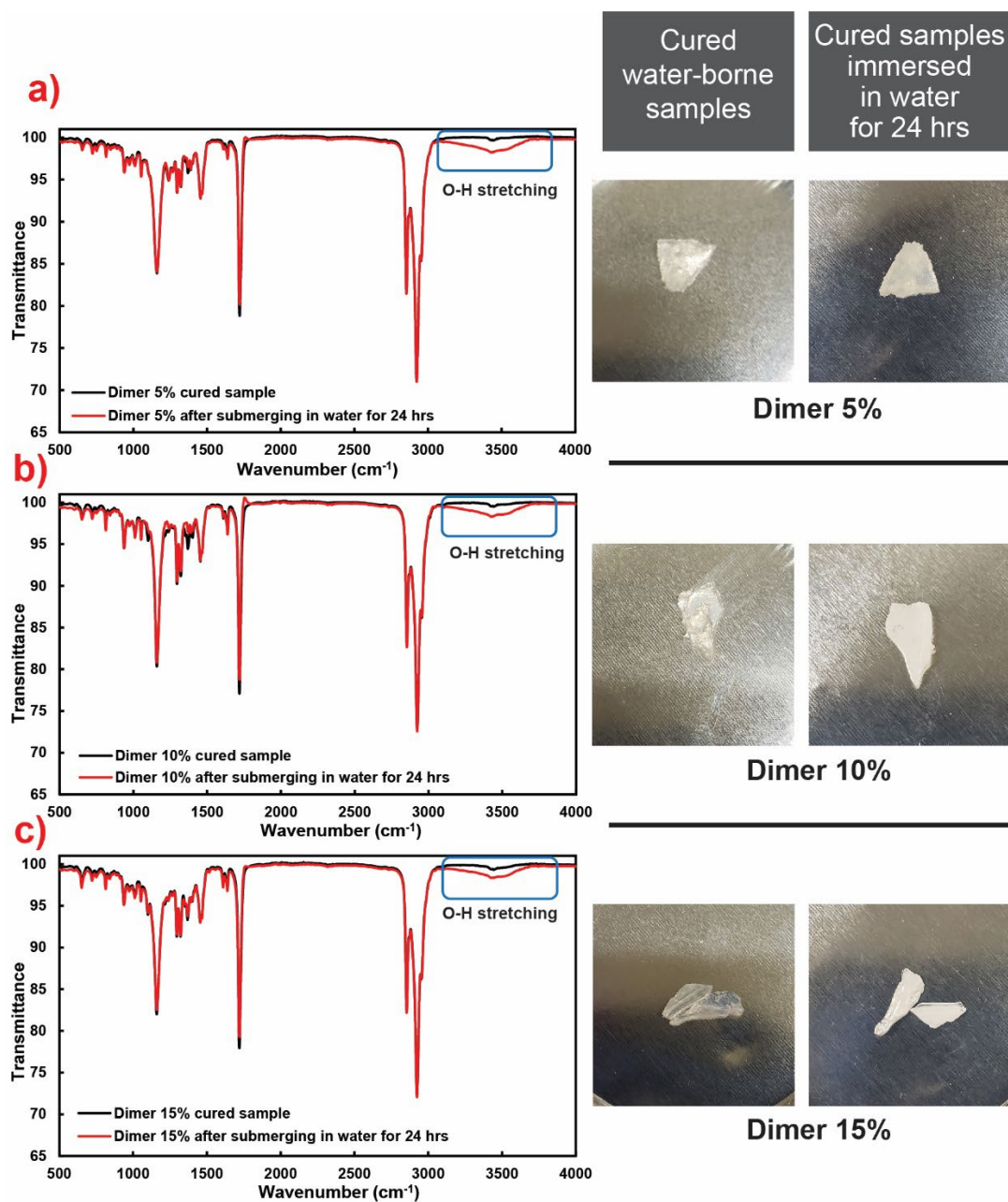


Figure 7. Cured polymers prepared by miniemulsion polymerization before and after submerging in water for 24 hours. FTIR spectra shows the completely cured samples (black line, —) and the

same sample after submerging in water for 24 hours (Red line, —). (a) Dimer 5% (b) Dimer 10% (c) Dimer 15%

It was observed that the samples containing higher molar ratios of BG dimer groups had a higher swelling ratio in the presence of water (Table S2, Supporting Information; the swelling ratios of Dimer 15% and 5% are 7.9 and 2.2%, respectively, after 24 hours at room temperature). This indicates an increase in water absorption for polymers with higher VPBA and GMMA content in the respective components. Boronic acids are highly hygroscopic¹⁵. However, in this study, the water absorption was limited through esterification with diol groups of GMMA prior to the miniemulsion polymerization, along with the use of highly hydrophobic monomers of IBOMA and C13MA.

Thermal properties of polymers and blends

Thermal properties of water-borne polymer resins were investigated by DSC and TGA and the results were listed in Table 2. Figure 8 exhibits the DSC traces for three samples containing (VPBA+GMMA) dimers. A melting point (T_m) was observed for the samples at -25 to -29 °C due to the presence of crystallizable C13MA in the polymer chains^{22, 56}. T_m s were previously observed for polymers with different dynamic cross-linking bonds (e.g. vitrimers)^{57, 58}. Considering the literature values of $T_{g,poly(IBOMA)} \approx 110-200$ °C^{18, 19} and $T_{g,poly(C13MA)} = -46$ °C^{18, 59}, the low T_m s were expected as similar IBOMA/C13MA copolymers with 20-40 mol% IBOMA in the initial feed prepared in miniemulsions had T_g s in the range of -17 to -52 °C²². T_m s were previously detected for statistical copolymers containing C13MA prepared in miniemulsion^{22, 56}. For IBOMA/C13MA copolymer with 18% IBOMA in polymer composition, a T_m at -33 °C was indicated²². It should be noted that the existence of DOWFAX 8390, n-hexadecane and unreacted C13MA monomers

in the dried samples caused some plasticizing effect and further depressed the T_m ^{22, 60, 61}. For this study, it can be assumed that increasing the amount of GMMA ($T_{g,poly(GMMA)} = 84\sim 106\text{ }^{\circ}\text{C}$)^{62, 63} and VPBA ($T_{g,poly(VPBA)} = 198\text{ }^{\circ}\text{C}$)^{64, 65} (herein dimer of GMMA and VPBA) in the initial monomer mixture can result in slightly higher T_g or T_m of polymers. However, it was not the case for Dimer 5 to 15% samples due to the different $\frac{[C13MA]_0}{[IBOMA]_0}$, different $M_{n,final}$ and $\bar{D}$ of polymer chains and non-identical concentration of residual unreacted monomers, especially C13MA, trapped within the polymer cross-linked network (see X values reported in Table 1). The T_g of samples was not detected because the T_g was probably below $-25\text{ }^{\circ}\text{C}$ and the polymers were effectively plasticized with the unreacted monomers present. Additionally, the fraction of cross-linked materials may have made segmental motion difficult and thus harder to detect the T_g .

TGA was carried out on samples to examine the thermal stability of polymers containing (GMMA+VPBA) dimers. The TGA traces in Figure 9 demonstrated a multi-stage decomposition of polymers versus temperature. The decomposition of unreacted monomers occurs at temperatures below $200\text{ }^{\circ}\text{C}$, causing an increase in decomposition rate (i.e. formation of a peak in derivative weights ($\%/^{\circ}\text{C}$) versus temperature graphs, Figure 9). The first decomposition temperature ($T_{dec,1}$, 10% weight loss) might correspond to the breakage of dynamic covalent bonds within the BG dimers and the last stage suggests the cleavage of the O-isobornyl bond in IBOMA and the formation and elimination of camphene at higher temperatures^{24, 66}. According to the results, $T_{dec,1S}$ for Dimer 5, 10 and 15% are slightly lower than the $T_{dec,1S}$ for IBOMA/C13MA copolymers with the same monomer ratios prepared in miniemulsion²². This decrease in $T_{dec,1S}$ is even higher if it is compared to our previous results on boronic ester cross-linked polymer blends with similar monomer compositions ($\Delta T_{dec,1}$ up to $104\text{ }^{\circ}\text{C}$)¹⁷. The difference in $T_{dec,1S}$ is due to the presence of unreacted monomers, surfactant and co-stabilizer within the polymer chains. The

decomposition temperatures at highest weight loss ($T_{\text{dec,max}}$) for the prepared samples were significantly higher than the IBOMA/C13MA copolymers with similar compositions ($\Delta T_{\text{dec,max}}$ up to 121 °C). This suggests that the addition of VPBA and GMMA to the polymer resins can improve the $T_{\text{dec,max}}$ of polymer resins^{22, 23}.

Increasing the initial BG dimer content (probably the cross-linking density) enhanced thermal stability of the polymers. This can be observed from the overall shift of the TGA curve to higher temperatures with increasing the BG dimer content (Figure 9 (d)) and comparatively higher ash content (ash content of Dimer 15% = 1.65 wt%; Dimer 10% = 0.72 wt% and Dimer 5% = 0.93 wt%). Furthermore, comparison of the decomposition temperatures for 50% weight loss ($T_{\text{dec,50\%}}$) of the polymer samples confirms the improvement of heat resistance with increasing the ratio of BG dimer in the initial hydrophobic mixture ($T_{\text{dec,50\%}}$ for Dimer 5, 10 and 15% were listed in Table 2).

Table 2. Thermal characterization of polymers and polymer blends.

Experiment ID	$M_{n,\text{final}}$ (kg mol ⁻¹)	T_m^a (°C)	$T_{\text{dec},1}^b$ (°C)	$T_{\text{dec},50\%}^b$ (°C)	$T_{\text{dec,max}}^b$ (°C)	$T_{\text{dec},2}^b$ (°C)
Dimer 5%	40.6	-25	197	338	417	487
Dimer 10%	37.8	-28	176	357	426	486
Dimer 15%	48.8	-29	196	369	403	471

^a T_m (melting point) measured by DSC under nitrogen atmosphere using three scans per cycle (heat/cool/heat) at a heating rate of 20 °C min⁻¹ and cooling rate of 50 °C min⁻¹ in the range of -90 to 120 °C.

^b $T_{\text{dec},1}$ ($T_{10\%}$ or onset of decomposition), $T_{\text{dec},50\%}$ (temperatures for 50% weight loss), $T_{\text{dec,max}}$ (temperature at which highest weight loss occurs) and $T_{\text{dec},2}$ (end of decomposition) measured by TGA under nitrogen atmosphere at a ramp rate of 15 °C min⁻¹.

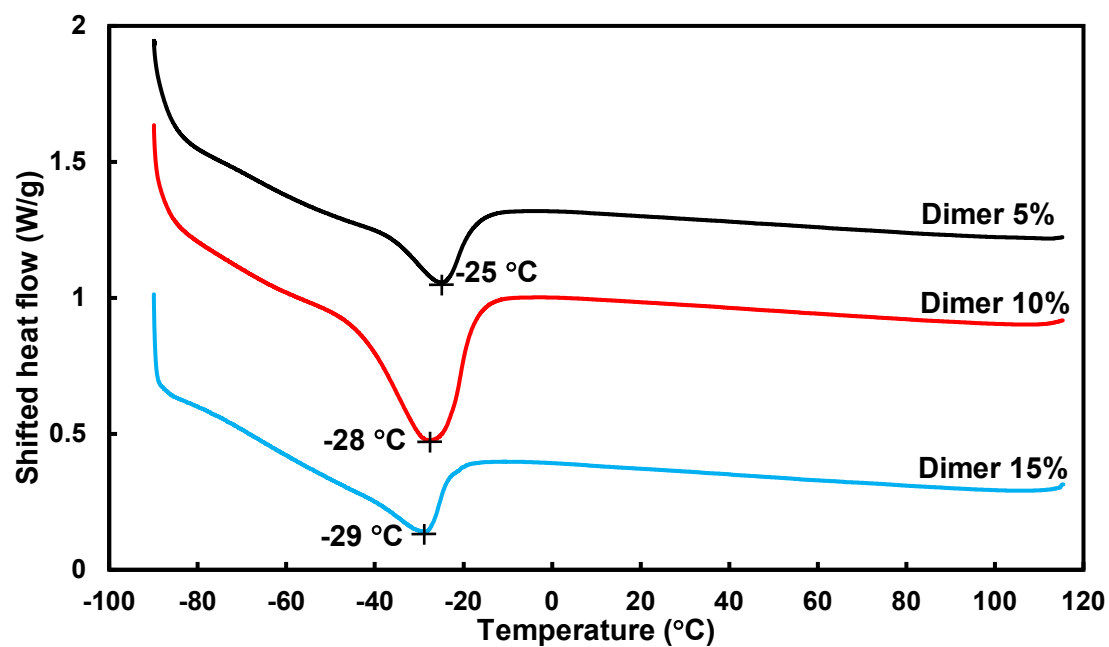


Figure 8. DSC traces for Dimer 5-15% samples in the temperature range of -90 to 120 °C. 2nd heating cycle in heat/cool/heat method with heating rate = 20 °C min⁻¹ and cooling rate = 50 °C min⁻¹.

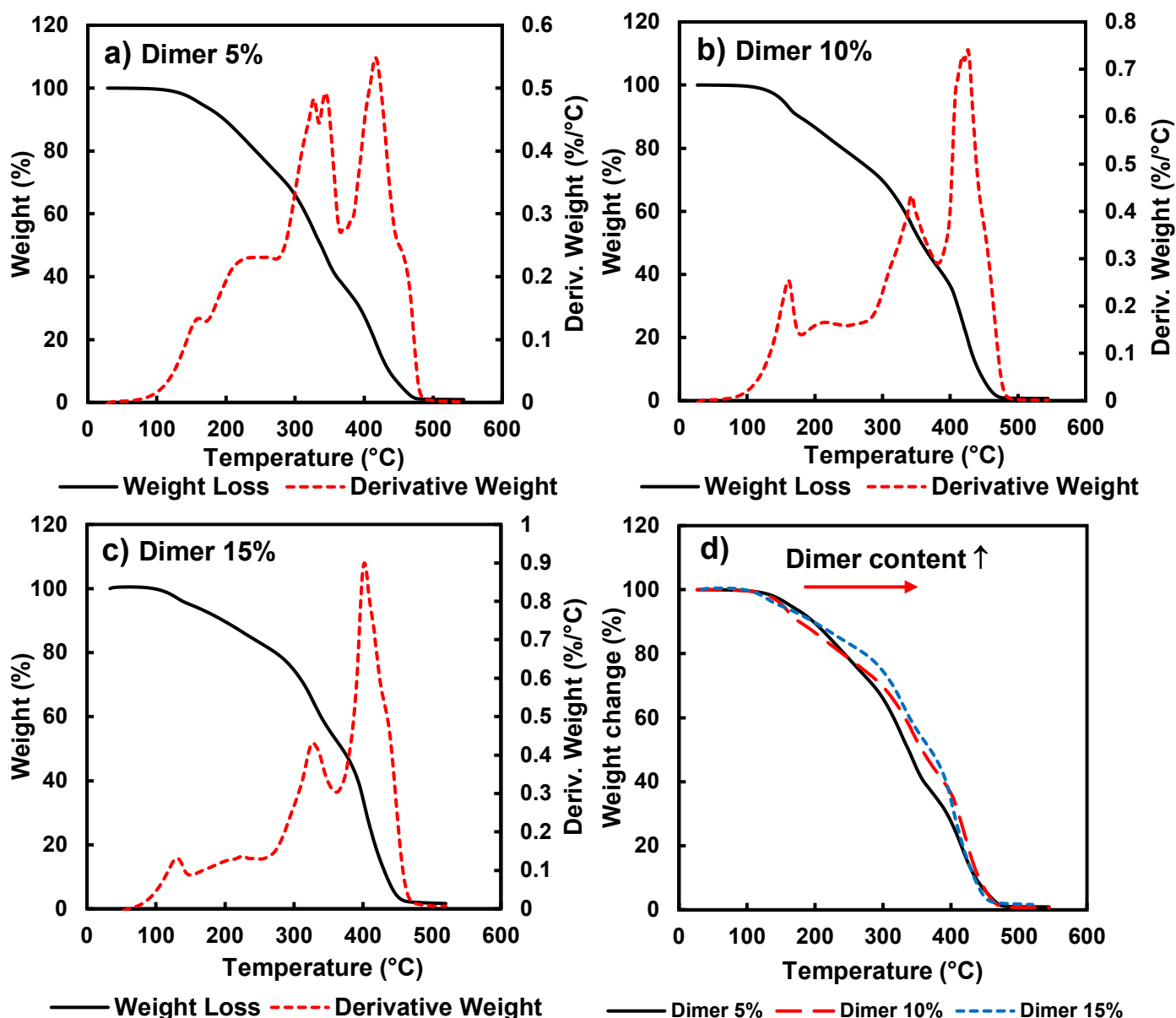


Figure 9. TGA traces for a) Dimer 5% b) Dimer 10% c) Dimer 15% d) comparison of decomposition properties for Dimer 5% (black line, —); Dimer 10% (Red line, - -); Dimer 15% (blue line, - -) samples. Increasing the BG dimer content slightly increased the thermal stability of the polymers. The samples were heated under the N₂ atmosphere with the heating rate of 15 °C min⁻¹. The polymers were completely dried under a fume hood at room temperature for 5 days before TGA.

De-crosslinking of polymers with pinacol

The dynamic covalent bonds of boronic esters can be easily cleaved in the presence of a diol-functionalized molecule¹⁷. Herein, the de-crosslinking of samples was conducted using pinacol in 1,4-dioxane. It was previously shown that the IBOMA/C13MA/VPBA and IBOMA/C13MA/GMA copolymers are completely soluble in 1,4-dioxane¹⁷. To better examine the effect of pinacol on solubility of samples, control samples were used in a similar test condition without the addition of pinacol. As seen in Figure 10, the samples were dissolved completely within 4 hours at 50 °C using pinacol (above the T_g of the samples). Without the addition of pinacol (control samples), 70.7 wt%, 66.0 wt% and 65.8 wt% of the total weight of the respective Dimer 5%, 10% and 15% samples remained insoluble. In addition, the swelling ratio of the control samples submerged in 1,4-dioxane for 24 hours revealed a high swelling ratio of polymers (up to 111.6%) (Table S2, Supporting Information). The swelling ratio decreased by increasing the initial BG dimer content from 5% to 15% (i.e. cross-linking density).

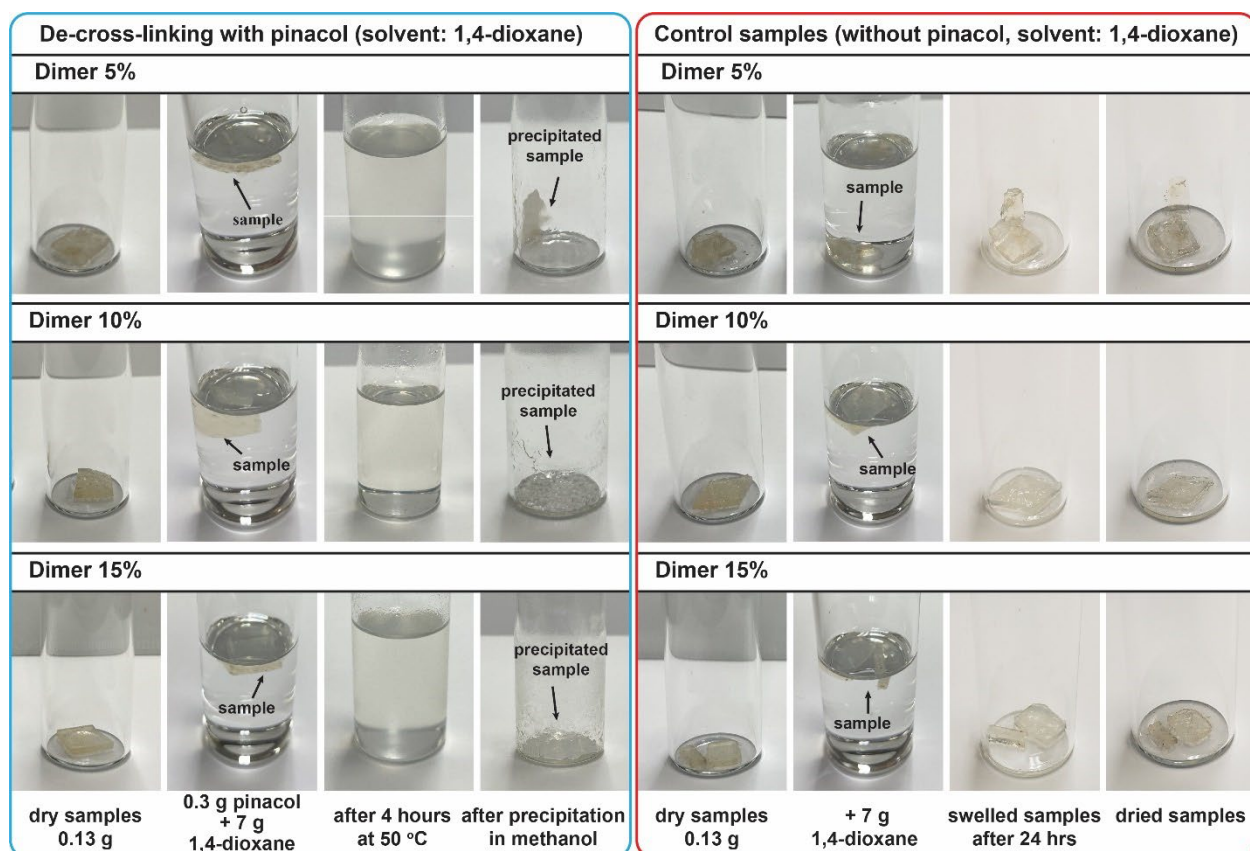


Figure 10. De-crosslinking of polymer samples using pinacol in 1,4-dioxane after 4 hours at 50 °C.

CONCLUSIONS

To prepare polymer resins with recyclability, the nitroxide-mediated polymerization of IBOMA and C13MA with 5-15 mol% VPBA and GMMA in initial feed (for the formation of boronic ester dynamic cross-linking) was conducted in a dispersed aqueous medium. To introduce moisture-activated dynamic cross-linking, a VPBA+GMMA dimer was formed and then added to increase the hydrophobicity of these monomers and thus incorporate them more easily into the monomer droplets. The nitroxide-mediated miniemulsion polymerization of IBOMA, C13MA with three different ratios of BG dimer (5%, 10% and 15%) was conducted using Dispolreg 007 alkoxyamine at 90 °C. Later, after the latex dried, the boronic ester dynamic cross-linking bonds formed. The

formation of cross-linking bonds was confirmed by FTIR and rheological measurements. The recyclability of samples was investigated by performing three recycling stages and comparing the mechanical properties of recycled samples with the original ones. The results suggested a higher stiffness (i.e. Young's modulus) for original and recycled samples containing higher BG dimer contents (Young's modulus for Dimer 5%, 10% and 15% is 0.23-0.34 MPa, 0.48-0.67 MPa and 12.39-22.85 MPa). The dried polymers, prepared in miniemulsion, can absorb toluene up to 266% of their initial weight in less than 300 minutes (ultimate swelling ratio up to 153%). However, a negligible water absorbance was observed for samples (less than 7.9 wt%). The T_{ms} of polymers were in the range of -29 to -25 °C and T_{dec} s showed the negligible effect of boronic ester cross-linking density on thermal stability of polymers. However, the heat resistance of polymers improved significantly compared to IBOMA/C13MA copolymers due to the presence of VPBA and GMMA monomers in the chains. Lastly, the chemical de-crosslinking of boronic ester bonds in polymers were examined by the addition of pinacol at 50 °C. It was shown that the samples can be completely dissolved in 1,4-dioxane within 4 hours due to the esterification of VPBA with pinacol.

MATERIALS AND METHODS

Materials

Isobornyl methacrylate (IBOMA, >99%, VISOMER® Terra IBOMA) and C13 methacrylate (C13MA, C13,0 alkyl methacrylate, >99%, VISOMER® Terra C13,0-MA) were provided from Evonik. IBOMA and C13MA were purified by passing them through a column containing basic alumina (Brockmann, Sigma Aldrich) and calcium hydride (5 wt% of basic alumina, Alfa Aesar) to remove the MEHQ inhibitor. 4-Vinylphenylboronic acid (VPBA, $\geq 97\%$) was purchased from

Oakwood Chemical. Glycerol monomethacrylate (GMMA, mixture of isomers, $\geq 95\%$) was purchased from Polysciences. DOWFAX™ 8390 (contains Disodium hexadecyldiphenyloxide disulfonate, disodium dihexadecyldiphenyloxide disulfonate, sodium sulfate, sodium chloride and water) was received from the Dow Chemical Company and used as the surfactant for emulsion polymerization. N-hexadecane (99%, Sigma Aldrich) was used as the co-stabilizer for emulsion system. 1,4-Dioxane (p-dioxane, $\geq 99\%$) was received from MilliporeSigma. HPLC grade Tetrahydrofuran (THF, 99.9%), methanol (MeOH, $>99\%$), methylene chloride (DCM, $\geq 99.5\%$) and toluene ($>99\%$) were purchased from Fisher chemical. 3-(((2-Cyanopropan-2-yl) oxy) - (cyclohexyl) amino)-2, 2-dimethyl-3-phenylpropanenitrile (Dispolreg 007) alkoxyamine was synthesized in our lab based on the Ballard et al procedure³⁰. Pinacol (98%) and molecular sieves (3 Å, pellets, 1.6 mm) were obtained from Sigma Aldrich. All the reactions, thermogravimetric analyses and rheological measurements were conducted under the high purity nitrogen (99.99%, Praxair).

Methods

The number average molecular weight (M_n) and dispersity (D) were measured by gel permeation chromatography (GPC, Waters Breeze). The instrument was equipped with 1 guard column and 3 Styragel® GPC columns (Waters) of HR1 (100 Å, M_n range of 100 to 5×10^3 g mol⁻¹), HR2 (500 Å, M_n range of 500 to 2×10^4 g mol⁻¹) and HR4 (10-4 Å, M_n range of 5×10^3 to 6×10^5 g mol⁻¹) and a differential refractive index RI 2414 detector. To prepare the samples for GPC, approximately 1 ml of polymer latex was dissolved in HPLC grade THF. The polymers were dissolved completely in THF and no sign of precipitation was observed. This was due to some water from the miniemulsion permitting the reversible opening of the boronic ester groups. The M_n of samples was determined relative to PMMA standards (calibration was done based on Varian

polymer standards with the molecular weight ranges of 875 to 1677000 g mol⁻¹) in HPLC grade THF at 40 °C.

The monomer conversion (X) was estimated using the area under the GPC peaks for monomers and polymer chains divided by the respective refractive index increments (dn/dc)⁶⁷. This was permissible as the peaks were well separated and the monomers were sufficiently high in molecular weight to be distinct from solvent peaks. The dn/dc value for poly(IBOMA) in THF is 0.108 ml g⁻¹⁶⁸. The dn/dc value for C13MA (monomer and homopolymer) is not available in literature. However, the dn/dc of C13MA and its polymer can be reasonably estimated from the dn/dc of similar alkyl methacrylates. The dn/dc for poly(octadecyl methacrylate) (C18MA) and poly(n-decyl methacrylate) (C10MA) in THF were 0.075 and 0.076 ml g⁻¹, respectively^{69, 70}. The dn/dc for heptadecanyl methacrylate (C17MA) in THF at 35 °C is 0.078 ml g⁻¹⁷¹. Previously, it was shown that the dn/dc of copolymers can be expressed from the following equation^{72, 73}:

$$\left(\frac{dn}{dc}\right) = w_i \left(\frac{dn}{dc}\right)_i + w_j \left(\frac{dn}{dc}\right)_j \quad (1)$$

where w_i and w_j are the weight fractions of monomers (i and j) in polymer resins and $\left(\frac{dn}{dc}\right)_i$ and $\left(\frac{dn}{dc}\right)_j$ are the refractive index increments for i and j homopolymers, respectively. Here, we assumed that the synthesized polymer resins are essentially the copolymers of IBOMA and C13MA (i is IBOMA and j is C13MA) and $\left(\frac{dn}{dc}\right)_{C13MA} \approx \left(\frac{dn}{dc}\right)_{C10MA} = 0.076 \text{ ml g}^{-1}$. Based on equation (1), the $\left(\frac{dn}{dc}\right)$ for Dimer 5% to 15% was calculated as 0.084-0.085 ml g⁻¹. Due to the similar dn/dc values for these systems, we assumed an equal dn/dc value for GPC peaks to estimate the monomer conversion.

FT-IR Spectrometry

The FTIR spectra were recorded in the range of 400-4000 cm^{-1} by a PerkinElmer Spectrum 2 with a single-bounce diamond and attenuated total reflectance (ATR) accessory.

Dynamic Light Scattering

The dynamic light scattering (DLS) test was performed using a Malvern Zetasizer nano-ZS, equipped with a 4 mW He-Ne laser at 633 nm. The photodiode detector had the angle of 173° and the measurement temperature was at 25°C . The samples were diluted to the concentration of 0.01-1000 mg ml^{-1} with R.O water before the measurements. The Z-average size was the average of 5 measurements.

Solid-State NMR

Solid-state ^{11}B and ^{13}C NMR spectra were obtained with a VNMRS 400 widebore NMR spectrometer operating at 100.5 MHz in a 4 mm Varian Chemagnetics double-resonance probe. The spectrums were acquired using multiple cross polarization (multiCP)⁷⁴ in 2048 scans and a 4 s recycle delay with 10 CP periods each of 1 ms, with 0.5 s between them, during spinning at 8 kHz. The multiCP spectrum of Dimer 15% was compared with a pulse-acquire spectrum using a recycle delay of 60 s and 2048 scans to verify that the spectra were quantitative. The ^{13}C spectra are referencing using glycine at 176.4 ppm wrt TMS and borax was used as the standard for the solid-state ^{11}B NMR setup.

Differential Scanning Calorimetry

DSC was carried out on the samples using a TA Instruments DSC Q2000. The (heat/cool/heat) method with heating rate of $20^\circ\text{C min}^{-1}$ was performed on samples in the temperature range of -

90 to 120 °C under nitrogen. The T_m s were measured in the second heating cycle by inflection method.

Thermogravimetric Analysis

Decomposition temperatures (T_{dec} s) of polymer samples were measured by thermogravimetric analysis (TGA, TGA Q500TM, TA Instruments) under the nitrogen (99.99%) at ramp rate of 15 °C min⁻¹ from 25 to 550 °C in aluminum pans.

Tensile Tests

Tensile tests were performed on an EZ-test-500N Shimadzu tensile tester at room temperature and ambient relative humidity ($T = 19.1$ - 23.9 °C, relative humidity of 38-58%). To check the temperature and relative humidity during the test, Fisherbrand™ Traceable™ digital humidity and temperature meter (Fisher Scientific, temperature range of -10 to 60 °C and accuracy of ± 1 °C; relative humidity range of 20 to 95% with the accuracy of $\pm 3\%$ for mid-range and $\pm 5\%$ elsewhere) was used. All dog-bone shaped samples were prepared in a hot press (Carver Manual Hydraulic Press with Watlow Temperature Controllers, Carver Inc., Wabash, IN, USA) at 80 °C. Three cycles of hot pressing were performed to avoid the formation of air bubbles in samples. In the first cycle, the polymer mixtures were heated to 80 °C under 6-8 metric tons pressure for 10 minutes. Next, two cycles of hot pressing were carried out at 20 psi and 80 °C for 15 minutes and 20 minutes, respectively. The samples were cooled down and were tested for tensile properties following the ASTM D638 type V standard. The samples were extended at a rate of 5 mm min⁻¹ and the reported data are the average of 5 measurements. To check the tensile results for recycled samples, dog-bone shaped samples were ground to small pieces and the same hot pressing procedure was applied to them for each recycling cycle.

Rheological Measurements

Oscillatory frequency sweep and dynamic mechanical analysis (DMA) were performed on an Anton Paar MCR 302 rheometer connected to a CTD 450 convection oven. For frequency sweep, the test was conducted on the samples between two parallel plates (diameter, 25 mm) in the frequency range of 1 to 1000 rad s⁻¹ with a constant amplitude of 1% under the pure nitrogen atmosphere (purity = 99.99%) at 80 °C. DMA was carried out on samples under the pure nitrogen atmosphere (purity = 99.99%) in the temperature range of 25-80 °C. A dynamic shear strain of 0.1% was applied for DMA experiments. For DMA, rectangular bars (60mm×10mm×2mm) prepared using the same hot pressing procedure (three cycles, 80° C) mentioned earlier in Tensile Test section.

Swelling Tests

The cross-linking density of polymer samples were examined by immersing approximately 0.13 g of polymer samples (Dimer 5-15%) in toluene (7.0 g, 5385 wt% based on samples) for 24 hours. The drying procedure started with the slow removal of the excessive solvent (toluene) using a syringe. Then, the samples were dried inside a fume hood for 24 hours at room temperature. The samples were placed under vacuum at room temperature for another 24 hours to ensure complete removal of the toluene. It was previously observed that similar polymers without cross-linking (IBOMA/C13MA, IBOMA/C13MA/GMMA and IBOMA/C13MA/VPBA) are completely soluble in toluene^{17, 22, 23}. However, 53.45%, 56.28% and 63.63% of Dimer 5, 10 and 15% samples, respectively, were insoluble after one day. To further study the swelling properties of samples, a fully dried piece of each sample with defined weight was placed inside an aluminum pan and was

immersed with excessive amount of toluene. Next, the solvent was carefully removed, and the sample was dried using an extra-low lint Kimwipes® to measure the weight change of the samples.

Preparation of (VPBA+GMMA) Dimer for Miniemulsion System

To prepare the (VPBA+GMMA) dimer (i.e. BG dimer) for miniemulsion polymerization of monomers, a mixture of 1:1 molar ratio of VPBA:GMMA was dissolved in 5 times the weight of monomers (500 wt% based on the monomers) of DCM solvent and 50 wt% of 3 Å molecular sieves based on the monomers to remove the water from the system. The mixture was stirred for 48 hours at room temperature to complete the reaction. Finally, the mixture was filtered using a 0.2 µm filter and dried for 7 days. The schematic for the reaction is shown in Figure S8 (Supporting Information). The FTIR spectrum of (VPBA+GMMA) dimer (Figure S1, Supporting Information) shows the successful boronic ester formation.

Miniemulsion Polymerization of IBOMA/C13MA/VPBA/GMMA

The monomers, Dispolreg 007 alkoxyamine and 0.8 wbm% n-hexadecane were mixed for 30 minutes with a stirring from a magnetic stir bar. The hexadecane was added as the co-stabilizer to improve the stability of the latex and prevent the Ostwald ripening effect⁷⁵. The aqueous phase was prepared by dissolving 2 wbm% DOWFAX 8390™ anionic surfactant in water and stirring the resulting solution for 30 minutes. Then, two solutions were mixed together and stirred for 30 minutes to prepare the initial latex. The initial latex was sonicated for 10 minutes (cycle = 0.5 and amplitude = 70%) in an ice water bath to prepare a latex containing nano-meter sized particles. As an example, for Dimer 5% miniemulsion polymerization, the hydrophobic phase was prepared by mixing Dispolreg 007 (0.07 g, 0.2 mmol), IBOMA (2.57 g, 11.5 mmol), C13MA (6.71 g, 25.0 mmol), Dimer of VPBA and GMMA (0.52 g, 1.9 mmol) and n-hexadecane (0.08 g, 0.3 mmol)

without the addition of any organic solvents. The aqueous phase was a solution of Dowfax 8390 (0.20 g, 2wbm%) in water (30.44 g, 1691.2 mmol). All the miniemulsion polymerizations were conducted in a three-necked round-bottom glass flask connected to a reflux condenser. The reflux condenser circulates a solution of 25/75 w/w glycerol/water through the condenser at 3 °C. The flask was equipped with a thermal well and a magnetic stirrer bar. The temperature sensor was placed inside the thermal well and connected to the temperature controller to keep the reaction temperature at 90 °C. The glass flask was placed in a heating mantle and on a stirrer. The latex was added to the flask and sealed with rubber septa. The system was purged using an ultrapure nitrogen flow for 30 minutes before increasing the temperature to deoxygenate the system and prevent any side reactions. To start the polymerization, the latex was heated with the rate of 10 °C min⁻¹ to reach 90 °C, while the nitrogen purging continues during the polymerization. The starting time of polymerizations ($t = 0$) was considered at the point at which the reaction temperature reached 75 °C. The samples were taken periodically to study the kinetics of polymerization for each experiment. At the end of the polymerization, the system was cooled down to temperatures below 40 °C and the latex was subsequently removed from the flask.

De-crosslinking of Polymers with Pinacol

The de-crosslinking of polymers was performed by immersing samples (approximately 0.13 g) in a solution of pinacol (0.3 g, 2.54 mmol) and 1,4-dioxane (7.0 g, 79.45 mmol). A control experiment was done at the same time for each polymer samples (~ 0.13 g). The samples were immersed in 1,4-dioxane (7.0 g, 79.45 mmol) without the addition of pinacol. The samples containing pinacol were completely dissolved in dioxane, suggesting the complete opening of boronic ester cross-linking bonds. The GPC and ¹H NMR measurements were conducted on samples after precipitation in methanol and complete drying. The control samples remained at room temperature

for 24 hours. Then, the 1,4-dioxane was removed with a syringe. The control samples were dried in a fume hood for 24 hours and under vacuum for another 24 hours at room temperature. The insoluble fraction of samples in the control vials was measured by comparing the initial weight of samples with the weight of remaining polymer.

Supporting Information

FTIR for (VPBA+GMMA) dimer, Dimer 15% polymer latex drying process, FTIR for Dimer 5%-15%, ^{11}B and ^{13}C solid-state NMR for Dimer 5%-15%, FTIR for Dimer 5% after submerging in toluene for 24 hours, Reaction for preparation of (VPBA+GMMA) dimer, Tensile results and swelling ratios for Dimer 5-15%.

AUTHOR INFORMATION

Corresponding Author

Milan Marić - Department of Chemical Engineering, McGill University, 3610 University St. Montreal, H3A 0C5 Quebec, Canada; orcid.org/0000-0002-4984-8761;
Email: milan.marić@mcgill.ca

Authors

Saeid Tajbakhsh - Department of Chemical Engineering, McGill University, 3610 University St. Montreal, H3A 0C5 Quebec, Canada; orcid.org/0000-0003-4177-3272

Faezeh Hajiali - Department of Chemical Engineering, McGill University, 3610 University St. Montreal, H3A 0C5 Quebec, Canada; <https://orcid.org/0000-0003-1739-3966>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

McGill Engineering Doctoral Award (MEDA) scholarship from the Faculty of Engineering, McGill University, Natural Sciences and Engineering Research Council (NSERC CRDPJ 518396-17 with Safran Cabin) and PRIMA Quebec with Safran Cabin (Project # R15-46-004) are

gratefully acknowledged for their financial support. We also thank the Centre Québécois sur les Matériaux Fonctionnels (CQMF) for the use of the DSC and TGA.

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Graphical Abstract

