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Robust Crosslinked Stereocomplexes and C₆₀ Inclusion Complexes of Vinyl-Functionalized Stereoregular Polymers Derived from Chemo/Stereoselective Coordination Polymerization

Fernando Vidal,[†] Laura Falivene,[‡] Lucia Caporaso,[§] Luigi Cavallo,^{*,‡} and Eugene Y.-X. Chen^{*,†}

[†] *Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872, USA*

[‡] *King Abdullah University of Science and Technology (KAUST), Physical Sciences and Engineering Division, Kaust Catalysis Center, Thuwal 23955-6900, Saudi Arabia*

[§] *Dipartimento di Chimica e Biologia, Università di Salerno, Via Papa Paolo Giovanni II, I-84084, Fisciano, Italy*

ABSTRACT: The successful synthesis of highly syndiotactic polar vinyl polymers bearing the reactive pendant vinyl group on each repeat unit, which is enabled by perfectly chemoselective and highly syndiospecific coordination polymerization of divinyl polar monomers developed through this work, has allowed the construction of robust crosslinked supramolecular stereocomplexes and C₆₀ inclusion complexes. The metal-mediated coordination polymerization of three representative polar divinyl monomers, including vinyl methacrylate (VMA), allyl methacrylate (AMA), and *N,N*-diallyl acrylamide (DAA) by C_s-ligated zirconocenium ester enolate catalysts under ambient conditions exhibits complete chemoselectivity and high stereoselectivity, thus producing the corresponding vinyl-functionalized polymers with high (92% *rr*) to quantitative (>99% *rr*) syndiotacticity. A combined experimental (synthetic, kinetic, and mechanistic) and theoretical (DFT) investigation has yielded a unimetallic, enantiomorphic-site controlled propagation mechanism. Post-functionalization of the obtained syndiotactic vinyl-functionalized polymers via the thiol-ene click and photocuring reactions readily produced the corresponding thiolated polymers and flexible crosslinked thin film materials, respectively. Complexation of such syndiotactic vinyl-functionalized polymers with isotactic poly(methyl methacrylate) and fullerene C₆₀ generates supramolecular crystalline helical stereocomplexes and inclusion complexes, respectively. Crosslinking of such complexes afforded robust crosslinked

* Corresponding author. E-mails: luigi.cavallo@kaust.edu.sa; eugene.chen@colostate.edu

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2
3 stereocomplexes that are solvent resistant and also exhibit considerably enhanced thermal and mechanical
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5 properties as compared to the uncrosslinked stereocomplexes.
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10 **Introduction**

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12
13 Owing to its unique feature that each enchaining monomer must be coordinated to the catalyst site,
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15 which can be rationally designed by tuning the electronic, steric, and symmetry properties of the ancillary
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17 ligand, metal-mediated coordination polymerization has evolved into arguably the most powerful
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19 technique for precisely controlling the polymerization stereochemistry.¹ In the case of vinyl monomers—
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21 a class of the technologically most important monomers, the metal-mediated coordination polymerization
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23 can be categorized into coordination-insertion polymerization, typically for catalytic polymerization of
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25 nonpolar olefins as well as copolymerization of nonpolar and polar olefins,² and coordination-addition
26
27 polymerizations, commonly for living or quasi-living and stereospecific polymerization of conjugated
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29 polar olefins such as acrylic monomers.^{3,4}
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33 Specifically focusing on polar divinyl monomers, rendering their chemoselective polymerization is
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35 important for the synthesis of vinyl-functionalized polymers, which can be post-functionalized—through
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37 the retaining vinyl groups attached to the main chain—into a variety of useful functional materials.⁵
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39 However, polymerization of such monomers with complete chemoselectivity by safeguarding one of the
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41 reactive vinyl groups while selectively polymerizing the other has been a challenging task for the radical
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43 polymerization (especially during the later stage),⁶ group-transfer polymerization,⁷ or anionic
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45 polymerization carried out at −20 °C or above.⁸ In the cases where complete chemoselectivity has been
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47 achieved utilizing the Lewis pair cooperativity in the Lewis pair polymerization,⁹ the resulting uncross-
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49 linked, soluble functional polymers exhibited a broad molecular weight distribution (*D*) and low
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51 tacticity,¹⁰ due to non-living and non-stereoselective features of this polymerization. In this context,
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53 coordination-addition polymerization of divinyl polar monomers is advantageous due to its high degree of
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control over polymerization characteristic, even at ambient temperature. For instance, the polymerization of allyl methacrylate (AMA) by half-metallocene yttrium catalysts was shown to be both living and chemoselective.¹¹ Furthermore, a chiral C_2 -ligated *ansa*-zirconocenium ester enolate complex, [*rac*- $C_2H_4(\eta^5\text{-indenyl})_2Zr(THF)]^+ [OC(O^iPr)=CMe_2][MeB(C_6F_5)_3]^-$ (**1**),¹² which is known to mediate stereospecific and living polymerization of simple alkyl methacrylates such as methyl methacrylate (MMA)^{12,13} and acrylamides,¹⁴ is not only completely chemoselective and living, but also highly isospecific, in the polymerization of polar divinyl monomers at ambient temperature.¹⁵ The origin of the perfect chemoselectivity and high isoselectivity arises from the catalyst site-controlled coordination-addition mechanism that dictates exclusive conjugate additions across the methacrylic double bond that is activated via coordination of the conjugated carbonyl to the cationic, chiral Zr center, thus leaving the pendant C=C bond intact.

Stereocomplexation between a pair of diastereomeric polymer chains of isotactic (*it*) and syndiotactic (*st*) poly(methyl methacrylate) (PMMA) in a typical 1/2 *it*-PMMA/*st*-PMMA ratio, when annealed in the solid state or crystallized in suitable solvents, generates a crystalline stereocomplex, *sc*-PMMA, representing a rare example of helical supramolecular structures based on a vinyl polymer.¹⁶ Polar donor solvents such as acetone, THF, DMSO and DMF are known to promote such stereocomplexation and thus referred as complexing solvents, while chlorinated solvents such as chloroform and dichloromethane decomplex the *sc*-PMMA polymer pair and are accordingly non-complexing or de-complexing solvents. Although the structure of *sc*-PMMA has received several revisions since the first report of the *sc*-PMMA structure model,¹⁷ its formation can be readily identified or characterized by gelation or precipitation of the crystalline complex in a complexing solvent, a high endothermic melting-transition temperature (T_m up to 210 °C) by differential scanning calorimetry (DSC), and a characteristic diffraction peak ($2\theta \sim 4.35^\circ$) by powder X-ray diffraction (pXRD).^{18,19} Worth noting here is that the formation of *sc*-PMMA was reported to be restricted to *it*-PMMA, but the ester group of the *st*-counterpart can be modified to extend to other *st*-poly(methacrylate)s.¹⁹ In addition, the formation

of *sc*-PMMA is not limited to the blending of the preformed *it*- and *st*-PMMA diastereomeric polymer pair, as *in situ* stereocomplexing polymerization of MMA using a pair of diastereospecific coordination polymerization catalysts has led to rapid, high-yield, ambient-temperature production of *sc*-PMMA with a high T_m of up to 217 °C.²⁰ Furthermore, supramolecular *sc*-PMMA/silicate nanocomposites²¹ were fabricated by mixing dilute THF solutions of *in situ* polymerized *it*-/*st*-PMMA/silicates,²² and crystalline hybrid polymer stereocomplexes between POSS (polyhedral oligomeric silsesquioxane) end-capped *it*- and *st*-PMMA-POSS chains were also synthesized.²³ Lastly, owing to its large helical cavity (~ 1 nm), syndiotactic *st*-PMMA, while does not crystallize by itself, co-crystallizes with specific organic solvents such as benzene²⁴ and encapsulates guest nanocages such as fullerenes C₆₀ and C₇₀²⁵ and MA-POSS²³ to form unique crystalline helical inclusion complexes.

In light of the above overviewed unique ability of highly syndiotactic *st*-PMMA to form helical supramolecular structures of stereo- and inclusion complexes, we hypothesized that highly syndiotactic vinyl-functionalized poly(methacrylate)s, synthesizable from the proposed chemoselective and syndiospecific coordination polymerization of divinyl monomers, should form stereocomplexes with *it*-PMMA and inclusion complexes with C₆₀ which, after crosslinking, should lead to robust, solvent and thermally resistant crosslinked stereocomplexes (Figure 1) and inclusion complexes. Such robust supramolecular stereocomplexes should solve the problem of decomplexation of the current stereocomplex and inclusion complex structures in non-complexing solvents and also enhance thermal and mechanical properties of the material. Accordingly, this report presents a full account of our work towards this central objective by first achieving chemoselective and syndiospecific polymerization of divinyl polar monomers to synthesize highly syndiotactic vinyl-functionalized polymers, next post-functionalizing and photocrosslinking such polymers into functional materials, and finally complexing such polymers to robust supramolecular stereo- and inclusion complexes followed by crosslinking.

Figure 1. Schematic representation of the *hypothesis* for stereocomplexation between syndiotactic acrylic polymers carrying pendant vinyl groups and *it*-PMMA and subsequent photocuring to robust crosslinked supramolecular structures.

Results and Discussion

Chemoselective and Syndiospecific Polymerization of Polar Divinyl Monomers. The first task of this study was to synthesize highly syndiotactic acrylic polymers carrying pendant vinyl groups via the development of chemoselective and syndiospecific polymerization. Previous reports from our group have shown neutral C_s -ligated zirconocene ester enolate complexes (pre-catalysts) such as $[\text{Ph}_2\text{C}(\text{Cp})(2,7\text{-}^t\text{Bu}_2\text{-Flu})]\text{Zr}[\text{OC}(\text{O}^i\text{Pr})=\text{CMe}_2]_2$ (**2**, $\text{Cp} = \eta^5\text{-cyclopentadienyl}$; $\text{Flu} = \eta^n\text{-fluorenyl}$), $[\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})]\text{Zr}[\text{OC}(\text{O}^i\text{Pr})=\text{CMe}_2]_2$ (**3**), and $[\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})]\text{ZrMe}[\text{OC}(\text{O}^i\text{Pr})=\text{CMe}_2]$ (**4**) can be readily activated with either $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (via hydride abstraction, followed by Michael addition), $\text{B}(\text{C}_6\text{F}_5)_3$ or $\text{THF}\cdot\text{B}(\text{C}_6\text{F}_5)_3$ (via methide abstraction), to generate the corresponding cationic complexes (catalysts) $2^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $3^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $4^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$, and $4^+(\text{THF})[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**5**, Scheme 1), respectively.²⁶ Such cationic complexes have been shown to promote rapid and syndiospecific polymerization of MMA at ambient temperature to produce highly syndiotactic *st*-PMMA with syndiotacticity up to 94% *rr*, proceeding through a monometallic, catalyst-site-controlled coordination-addition polymerization mechanism via eight-membered-ring ester enolate intermediates.²⁶ Accordingly, $2^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$,

$3^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $4^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (generated by in-reactor activation), and **5** (generated by pre-activation) were employed for the current investigation into the polymerization of the three representative polar divinyl monomers, AMA, vinyl methacrylate (VMA), and *N,N*-diallyl acrylamide (DAA), aiming to achieve chemoselective and syndiospecific polymerization of such monomers and thus produce the corresponding highly syndiotactic polar vinyl polymers carrying a pendant C=C bond in every repeat unit (Scheme 1).

Scheme 1. Chemoselective and syndiospecific polymerization of polar divinyl monomers as well as structures of monomers, catalysts, and polymers involved in this study.

Selected results for the polymerization of the three representative polar divinyl monomers by pre-catalysts **2–4** are summarized in Table 1. At the outset, control runs showed that neither the neutral pre-catalyst nor the activator itself exhibited any activity toward such monomers. In contrast, cationic

complexes $2^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $3^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, and $4^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$, derived from activation with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (for bis-enolate precatalysts **2** and **3**) or $\text{B}(\text{C}_6\text{F}_5)_3$ (for mono-enolate precatalyst **4**), are highly active, quantitatively chemoselective, and also syndiospecific for polymerizations of such polar divinyl monomers at ambient temperature. Starting with the AMA polymerization in CH_2Cl_2 at 25 °C, $3^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (0.5 mol% loading) afforded *st*-PAMA with a high syndiotacticity of $[rr] = 92.4\%$ and perfect chemoselectivity (Figure S2), but achieved a maximum monomer conversion of only 55% in 1 h (run 2). Cationic complex $4^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ performed similarly (run 3 vs. 2). Interestingly, $2^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, the more electron-rich and sterically encumbered catalyst with two substituted *tert*-butyl groups on the Flu ring, achieved a much higher monomer conversion of 92.7% and thus a higher molecular weight polymer ($M_n = 55.3$ kg/mol, $D = 1.33$), but it produced *st*-PAMA with a lower syndiotacticity of $[rr] = 87.9\%$ (run 1). The isolated *st*-PAMA ($M_n = 35.0$ kg/mol, $[rr] = 92\%$, run 2) is soluble in common organic solvents and exhibited a glass transition temperature (T_g) at 54 °C, as measured by DSC, which is considerably higher than the counterpart *it*-PAMA (−13 °C to 0 °C, in the order of increasing M_n).¹⁵ A thermal crosslinking exothermic peak with an onset temperature and a peak maximum of 142 °C and >200 °C, respectively, was also observed on the DSC curve.

Table 1. Polymerization of polar divinyl monomers (M) by precatalysts **2–4**^a

run no.	M	Pre-cat.	Activator	Temp (°C)	Time (min)	conv. ^b (%)	M_n^c (kg/mol)	D^c (M_w/M_n)	$[rr]^d$ (%)	$[mr]^d$ (%)	$[mm]^d$ (%)
1	AMA	2	$[\text{Ph}_3\text{C}][\text{B}]$	25	180	92.7	55.3	1.33	87.9	10.6	1.5
2	AMA	3	$[\text{Ph}_3\text{C}][\text{B}]$	25	60	55.1	35.0	1.56	92.4	6.0	1.6
3	AMA	4	$[\text{B}]$	25	60	53.0	24.5	1.32	90.7	7.4	1.9
4	VMA	2	$[\text{Ph}_3\text{C}][\text{B}]$	25	60	96.2	42.9	1.40	87.0	10.5	2.5
5	VMA	3	$[\text{Ph}_3\text{C}][\text{B}]$	25	30	98.3	42.5	1.38	92.4	7.0	0.6
6	VMA	4	$[\text{B}]$	25	30	98.5	41.2	1.36	93.0	6.4	0.6
7	VMA	4	$[\text{B}] \cdot \text{THF}$	25	10	100	42.5	1.36	93.5	6.1	0.4
8	VMA	3	$[\text{Ph}_3\text{C}][\text{B}]$	0	30	100	86.7	1.21	95.7	2.9	1.4
9	VMA	4	$[\text{B}] \cdot \text{THF}$	0	30	97.0	98.3	1.17	94.8	3.5	1.7
10	DAA	3	$[\text{Ph}_3\text{C}][\text{B}]$	25	10	89.0	47.5	1.34	>99	–	–
11	DAA	4	$[\text{B}] \cdot \text{THF}$	25	10	94.5	42.9	1.29	>99	–	–

^a Conditions: activator $[\text{Ph}_3\text{C}][\text{B}] = [\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, $[\text{B}] = \text{B}(\text{C}_6\text{F}_5)_3$; solvent (3.0 mL) CH_2Cl_2 for runs 1–9, toluene for runs 10 and 11; $[\text{M}]/[\text{cat}] = 200$; *pre-activation* method (pre-mixing of pre-catalyst with activator, followed by addition of monomer), except for runs #3 and #6 where the *in-reactor activation* method was used (pre-mixing of monomer with activator, followed by addition of pre-catalyst). ^b Monomer (M) conversion measured by ^1H NMR. ^c Number-average molecular weight (M_n) and dispersity (D) determined by gel-permeation chromatography (GPC) relative to PMMA standards. ^d Tacticity measured by ^1H or ^{13}C NMR in CDCl_3 .

Moving to VMA polymerization, all three C_s -ligated catalysts are perfectly chemoselective and highly syndiospecific. Again, the two catalysts without the *tert*-butyl substitution, $3^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and $4^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$, exhibited similar polymerization characteristics (run 5 vs. 6), including high activity (>98% conversion in 30 min), medium molecular weight ($M_n = 41.2\text{--}42.5$ kg/mol), medium dispersity ($D = 1.36\text{--}1.38$), and high syndiotacticity ($[rr] = 92.4\%$ and 93.0%). The polymerization by cation **5** $\{= 4(\text{THF})^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$, generated from the reaction of **4** + $\text{THF} \cdot \text{B}(\text{C}_6\text{F}_5)_3$, Scheme 1} was even more rapid, achieving 100% monomer conversion in only 10 min without signs of gel formation and also producing *st*-PVMA with a high syndiotacticity of $[rr] = 93.5\%$ (run 7). When the polymerization was carried out at 0°C , the molecular weight of the resulting polymer was much higher and the dispersity became narrower, while still achieving quantitative or near quantitative conversion: $M_n = 86.7$ kg/mol, $D = 1.21$, $[rr] = 95.7\%$ by $3^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (run 8); $M_n = 98.3$ kg/mol, $D = 1.17$, $[rr] = 94.8\%$ by **5** (run 9). The chemoselectivity of the VMA polymerization is also perfect, as revealed by complete disappearance of the methacrylic $=\text{CH}_2$ proton signals at δ 6.23 and 5.68 ppm and complete retention of the pendant vinyl group $-\text{CH}=\text{CH}_2$ proton signals centered at δ 7.14, 4.91, and 4.63 ppm (Figure 2), indicating that the polymerization proceeded exclusively through conjugate addition across the methacrylic double bond. Significantly, analysis of the triad stereoerrors of the resulting *st*-PVMA gave $2[mm]/[mr] \sim 1$ (0.97 for both runs 8 and 9), indicative of an enantiomorphic-site controlled mechanism. Furthermore, the ^{13}C NMR spectrum of the polymer in the $\text{C}=\text{O}$ pentad (*rrrr*) region provided collaborative evidence for the formation of the highly syndiotactic *st*-PVMA (Figure 3). DSC analysis of the highly syndiotactic *st*-PVMA showed a T_g of $\sim 100^\circ\text{C}$, which is considerably higher than *at*-PVMA ($44\text{--}49^\circ\text{C}$),¹⁵ as well as a thermal crosslinking exothermic peak with an onset temperature and a peak maximum of 153°C and 184°C .

°C, respectively. We also examined the degree of the polymerization control over molecular weight by varying the [VMA]/[5] ratio from 100 to 900 (0.11 mol% catalyst loading) in CH₂Cl₂ at ambient temperature, all of which runs proceeded to high conversions without signs of gel formation. The M_n value of the resulting *st*-PVMA increased linearly ($R^2 = 0.992$) from 29.6 kg/mol ($\bar{D} = 1.28$) to 164 kg/mol ($\bar{D} = 1.48$, Figure 4) as the [VMA]/[5] ratio was increased from 100 to 900, showing the ability of this polymerization system to control the resulting polymer molecular weight while maintaining the relatively low dispersity.

Figure 2. Overlay of ¹H NMR (CDCl₃, 25 °C) spectra of VMA and *st*-PVMA.

Figure 3. ^{13}C NMR spectra (CDCl₃, 50 °C) showing the C=O pentad (*rrrr*) region of *st*-AMA (left, run 2), *st*-PVMA (center, run 8) and *st*-PDAA (right, run 10).

Figure 4. Plots of M_n (kg/mol or kDa) and D (shown in parenthesis) of *st*-PVMA produced by **5** vs. [VMA]₀/[**5**]₀ ratio (CH₂Cl₂, 23 °C).

The chemoselectivity and stereospecificity of $3^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and **5** toward the polymerization of DAA were also carefully examined. Remarkably, this polymerization not only was rapid, achieving 89.0% (run 10) and 94.5% (run 11) conversions in 10 min, it also exhibited both *quantitative chemoselectivity* (Figure S3) and *syndiospecificity* ($[rr] > 99\%$, Figure 3). DSC analysis of the highly syndiotactic *st*-PDAA showed a T_g of 35.8 °C as well as a thermal crosslinking exothermic peak with an onset temperature and a peak maximum of 216 °C and 290 °C, respectively. Worth noting also is that *st*-PDAA is soluble in common solvents of a wide polarity range, including MeOH, DMF, THF, acetone, CHCl₃, Et₂O, and toluene, whereas *it*-PDAA is found soluble only in limited solvents such as CHCl₃ and CH₂Cl₂. In comparison, the initiator efficiency (I^*), calculated as $I^* = M_n(\text{calcd})/M_n(\text{exptl})$, where $M_n(\text{calcd}) = \text{MW}(\text{M}) \times [\text{M}]_0/[\text{Zr}]_0 \times \text{conversion \%} + \text{MW of chain-end groups}$, was in the range of 43–55 % for AMA polymerization at RT, 51–54 % for VMA polymerization at RT, and 57–67 % for DAA polymerization at RT.

Mechanism of Polymerization. Next, we examined the kinetics of VMA polymerization by catalyst **5**, revealing the polymerization is first-order with respect to monomer concentration [VMA] for all the six [VMA]₀/[**5**]₀ ratios investigated (150 to 500, Figure 5). A double logarithm plot (Figure 6) of the apparent rate constants (k_{app}), obtained from the slopes of the best-fit lines to the plots of $\ln([\text{VMA}]_0/[\text{VMA}]_t)$ vs. time, as a function of $\ln([\text{5}]_0)$, was fit to a straight line ($R^2 = 0.986$) with a slope of 1.1. Thus, the kinetic order with respect to [**5**], given by the slope of ~ 1 , reveals that the propagation is also first order in catalyst concentration. These results indicate that the resting state in the proposed monometallic propagation “catalytic” cycle (Scheme 2) is the cyclic ester enolate **B**, which was structurally modeled by the isolated cationic cyclic ester enolate complex **6** (*vide infra*), and that associative displacement of the coordinated ester group by incoming monomer to regenerate the active

species **A** (structurally modeled by complex **5**) is the rate-determining step (i.e., **B** $\rightarrow$ **A**, Scheme 2). These key features of the mechanism are the same as those already established for the coordination-addition polymerization of alkyl methacrylates.^{3b,13,26}

Figure 5. Semilogarithmic plots of $\ln\{[VMA]_0/[VMA]_t\}$ vs. time for the polymerization of VMA by **5** in CH_2Cl_2 at 23 °C. Conditions: $[VMA]_0 = 0.832$ M; $[5]_0 = 5.55$ mM (●), 4.16 mM (◇), 3.33 mM (▲), 2.77 mM (□), 2.07 mM (◆), 1.66 mM (○).

Figure 6. Plot of $\ln(k_{app})$ vs. $\ln([5]_0)$ for the VMA polymerization by **5** in CH_2Cl_2 at 23 °C.

Scheme 2. Proposed mechanism (propagation “catalytic” cycle) for the chemoselective and syndiospecific polymerization of VMA as well as the structures of **5** and **6** as synthetic structural models for active species **A** and resting state chelate **B**, respectively.

To provide further evidence to support the mechanism outlined in Scheme 2, cation **5** was reacted with 1 equiv of VMA to cleanly generate the corresponding single-monomer-addition product, the eight-membered metallacycle²⁷ resting intermediate $\{[\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})]\text{Zr}[\text{OC}(\text{OCH}=\text{CH}_2)=\text{CMeCH}_2\text{C}(\text{Me}_2)\text{C}(\text{O}^i\text{Pr})=\text{O}]\}^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**6**) (Figure 7). This intermediate can also be generated and isolated in >91% yield via the 1:1 ratio reaction of the pre-catalyst **4** with the borane-monomer adduct $\text{VMA}\cdot\text{B}(\text{C}_6\text{F}_5)_3$ (see the SI for procedures and characterizations). Likewise, the metallacycle corresponding to the first AMA addition intermediate $\{[\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})]\text{Zr}[\text{OC}(\text{OCH}_2\text{CH}=\text{CH}_2)=\text{CMeCH}_2\text{C}(\text{Me}_2)\text{C}(\text{O}^i\text{Pr})=\text{O}]\}^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**7**) was generated in the similar fashion (see the SI and Figure S4). The successful generation and isolation of the first-monomer-addition product **6**, serving as the structural model of the resting intermediate **B**, implies that the monomer addition is fast relative to the monomer coordination in the propagation “catalytic” cycle depicted in Scheme 2 (otherwise, only polymers or oligomers, plus the unreacted **5** or **4**, would be formed). Importantly, addition of excess of VMA to a solution of **6** brought about rapid polymerization of VMA into *st*-PVMA, thereby confirming cation **6** as the resting intermediate of the catalytic cycle by this kinetic competence check. Overall, all the experimental evidence to date is consistent with the polymerization mechanism depicted in Scheme 2.

Figure 7. ^{19}F NMR (top) and ^1H (bottom) spectra (CD_2Cl_2 , 25 °C, residual NMR labeled as *) of the isolated cationic complex **6**. Anion $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ omitted for clarity.

Mechanism of Stereoselection. Next, we investigated the mechanism of stereoselection by a computation study via DFT calculations. This needed study was prompted by an interesting observation that, while the polymerizations of AMA and VMA by the C_2 -ligated catalyst **1** were drastically different, leading to formation of highly isotactic PAMA with $[mm] = 95\text{--}97\%$ and isotactic-biased PVMA with $[mm] = 51\text{--}53\%$, respectively,¹⁵ both polymerizations of AMA and VMA by C_s -ligated catalysts afforded highly syndiotactic polymers, with even higher syndiotacticity of $[rr] = 94\text{--}96\%$ achieved for the VMA polymerization (*vide supra*). Thus, it is intriguing that the placement of the sp^3 -hybridized CH_2 group between the ester oxygen atom and the sp^2 -hybridized vinyl moiety in the case of AMA substantially enhanced the isospecificity of the polymerization but had no effect on (or even slightly reduced) the syndiospecificity of the polymerization, relative to VMA without the CH_2 group, highlighting the importance of the sterics and orientation of the ester OR group of the methacrylate monomer in the transition state (TS) structure that determines the stereospecificity of the metallocene-catalyzed polymerization.^{26a,28} Accordingly, DFT calculations were performed to provide a rationalization of the above experimentally observed high isospecificity in AMA polymerization and the low isospecificity in VMA polymerization by C_2 -ligated catalyst **1** (EBI-Zr) system, as well as the high syndiospecificity in both AMA and VMA polymerizations with C_s -ligated catalyst **5** $[\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{Zr}]$ system.

We calculated all the TSs for AMA and VMA additions involving the *re* and *si* prochiral faces of the growing chain by considering geometries where the pendant group of the monomer and of the chain are located on opposite sides (*trans*) or on the same side (*cis*) of the metallocene equatorial belt. In addition, for the C_2 -symmetric EBI-Zr system, the g^+ and g^- conformations of the metallocene bridge have been considered.²⁸ In all the geometries a *t*Bu group was used to model the remaining of the growing chain. For the sake of simplicity, we anticipate that with the (*S,S*)-EBI-Zr based system all competitive

geometries show a g^+ conformation of the metallocene bridge. The favored TS involves the *si* face of the chain and shows a *trans* geometry whereas the *cis* geometry is favored for the competitive *re*-face addition, with both monomers. Finally, with the (*S*)-Ph₂C(Cp)Flu-Zr system a *trans* geometry is favored in both TSs.^{26a,28}

The geometries and the corresponding free energy ΔG_{Stereo} (kcal/mol, DCM) of the competitive TSs are reported in Figure 8 for **1** and in Figure 9 for **5** with both monomers. Focusing on AMA addition, with **1** the TS involving the *si*-face of the growing chain is favored by a ΔG_{Stereo} of 5.6 kcal/mol (Figure 8a vs. 8b). Competition is with addition of the *re*-face, which is disfavored by steric repulsion between the 6-membered ring of the indenyl ligand and the -OR group of the growing chain. To alleviate this steric clash the pendant -OR group of the chain rotates away from the indenyl ligand resulting in a gauche conformation of the C1-C2-O3-C4 dihedral angle (Figure 8b). Differently, in the favored *si*-face addition TS the C1-C2-O3-C4 dihedral angle is much closer to the ideal *trans* value (Figure 8a). The high ΔG_{Stereo} of 5.6 kcal/mol is in qualitative agreement with the high isotacticity of the obtained PAMA.

Figure 8. Transition state geometries for the competitive addition at the *si* and *re* face of the growing chain for AMA (**a** and **b**) and VMA (**c** and **d**), respectively, with (*S,S*)-EBI-Zr system (**1**). The free energies (kcal/mol, DCM) are relative to the TS involving the *si* face of the growing chain (**a** and **c**). The dashed line indicates the emerging C–C bonds.

The competitive TSs geometries associated with VMA addition are compared in Figures 8c and 8d. In this case, addition of the *si*-face is favored by a ΔG_{Stereo} of 3.1 kcal/mol over addition of the *re*-face. As for AMA, the TS for addition of the *re*-face is disfavored by steric interaction between the pendant group of the chain and the indenyl ligand, resulting in a less stable conformation assumed by the growing chain, with a C1-C2-O3-C4 dihedral angle of 53° (Figure 8d). Although still rather large in absolute value, the ΔG_{Stereo} of 3.1 kcal/mol calculated for VMA is 2.5 kcal/mol lower than the ΔG_{Stereo} calculated for the AMA, in qualitative agreement with the observed much lower isotacticity of the produced PVMA. The lower stability of the favored *si*-face TS for VMA is responsible for the observed lower selectivity in the polymerization of VMA relative to AMA: the different nature of the ester carbon in the chain, sp^2 for VMA vs sp^3 for AMA, induces a different steric interaction between the chain and the metallocene skeleton, mainly in the favored *si*-face TSs (Figure 8a vs. 8c). In fact, despite the fact that the *si*-chain is located in the open part of the catalyst, being away from the 6-membered ring of the indenyl ligand, in the case of VMA the rigid $-\text{O}-\text{CH}=\text{CH}_2$ group is forced to be close to the 5-membered ring of the ligand (see short distances reported in Figure 8c). Conversely, in the case of AMA, the sp^3 ester carbon of the $-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2$ moiety allows the chain to rotate away from the 5-membered ring of the ligand, minimizing unfavorable interaction between the $-\text{OR}$ group of the growing chain and the metallocene skeleton (compare the value of 139° for the C2-O3-C4-C5 dihedral angle in the case of AMA vs. the value of -170° in the case of VMA in Figures 8a and 8c, respectively).

Moving to C_S -ligated catalyst **5**, with both monomers, the favored TS involves the *si*-face of the chain, which is located in an open part of the space away from the fluorenyl moiety of the ligand (Figures

9a and 9c). Steric interaction between the monomer and the metallocene skeleton can be observed for both AMA and VMA. The competitive *re*-face TSs are disfavored by steric interaction between the chain and the ligand (see the short distance in Figures 9b and 9d). The rather similar ΔG_{Stereo} of 2.7 kcal/mol and 2.2 kcal/mol, calculated for VMA and AMA, respectively, are in good agreement with the experimentally observed similar syndiotacticity of PVMA and PAMA (although the syndiotacticity of PVMA is somewhat higher than that of PAMA, *vide supra*).

Figure 9. Transition state geometries of the competitive addition at the *si* and *re* face of the growing chain for AMA (a and b) and VMA (c and d), respectively, with *(S)*-Ph₂C(Cp)Flu-Zr system (5). The free energies (kcal/mol, DCM) are relative to the TS involving the *si* face of the growing chain (a and c). The dashed line indicates the emerging C–C bonds.

Post-Functionalization and Photocrosslinking to Functional Materials. Post-functionalization of syndiotactic polymers bearing the pendant vinyl (–CH=CH₂) functional group on every repeating unit was performed through two approaches: the thiol-ene “click” reaction and photocuring. The former

approach has been widely used and proven to be highly effective for functionalization of ene-bearing polymers.²⁹ We first examined functionalization of *st*-PVMA ($M_n = 40.9$ kg/mol, $D = 1.19$) and *st*-PDAA ($M_n = 373$ kg/mol, $D = 1.43$) with two model thiols, 4-*tert*-butylbenzylmercaptan (RSH1) and 1-adamantanethiol (RSH2), using the click reaction with 2,2-dimethoxy-2-phenylacetophenone (DMPA) as the photoradical initiator under photochemical conditions (RT, UV lamp centered at $\lambda = 350$ nm) in chloroform (Scheme 3). The pendant vinyl groups were completely converted into new $-\text{CH}_2\text{CH}_2\text{-SR}$ groups, as confirmed by ^1H NMR spectra (Figure 10 & Figure S5), which also showed that the tacticity of the resulting thiolated polymers was the same as the parent polymers in all the cases. GPC analysis of the thiolated polymers, which are all soluble in chloroform, showed an increase in the M_n and D values (Figure S6), indicative of some degree of light crosslinking due to the non-selective radical initiation in the presence of the high concentration of reactive $\text{C}=\text{C}$ pendant groups. The thermal properties of the functionalized polymers were also significantly affected by the inclusion of the $-\text{SR}$ groups. For instance, the first-step onset decomposition temperature (T_d) of *st*-PVMA (234 °C) measured by thermal gravimetric analysis (TGA) was enhanced by 62 °C to $T_d = 296$ °C of both *st*-PVMA-SR1 and *st*-PVMA-SR2 (Figure S7), attributed to the transformation of the $-\text{OCH}=\text{CH}_2$ group into the $-\text{OCH}_2\text{CH}_2\text{SR}$ moiety, which was accompanied by a change in the T_g from 102 °C of *st*-PVMA to 39 °C and 118 °C of *st*-PVMA-SR1 and *st*-PVMA-SR2, respectively (Figure S8, top). In sharp contrast, *st*-PDAA exhibited a lower T_g (Figure S8, bottom), but high thermal stability than its thiolated polymers *st*-PDAA-SR1 and *st*-PDAA-SR2 (Figure S9).

Scheme 3. Post-functionalization of *st*-PVMA and *st*-PDAA via the thiol-ene "click" chemistry.

Figure 10. Overlay of ^1H NMR (CDCl_3 , 25 $^\circ\text{C}$) spectra of *st*-PVMA (bottom), *st*-PVMA-SR1 (top), and *st*-PVMA-SR2 (middle).

Owing to the presence of the pendant vinyl groups, *st*-PVMA can also be readily photocured into flexible thin films for examining their thermo-mechanical properties. Thus, a solvent casted *st*-PVMA film was subjected to controlled crosslinking conditions under UV (350 nm) photoradical initiation with DMPA inside a Luzchem photoreactor for 10 min, producing a flexible, translucent, colorless thin film (*st*-PVMA-*hν*, Figure 11). A crosslinker, 1,4-benzenedimethanethiol (RSH3), was also added in varied amounts (2.5, 5, and 10 mol%) to prepare films with increased crosslinking and brittleness as the amount of RSH3 increases. Dynamic mechanical analysis (DMA) showed an increase in T_g from the parent *st*-PVMA film (105 °C) to the photocured *st*-PVMA-*hν* film (111 °C) after 10 min of UV irradiation, which was accompanied by an increase in both storage modulus (E') and loss modulus (E'') in both glassy (values reported at 25 °C) and rubbery (values reported at 150 °C) states, Figure 12 and Table 2 (entry 2 vs. 1). A further increase in T_g (measured by the peak maxima of the $\tan \delta$ (E''/E') curve in the DMA analysis) to 112, 121, and 128 °C was observed when the amount of the added crosslinker RSH3 was increased from 2.5 to 5.0 to 10 mol%, respectively (Table 2). This observed increasing T_g trend is a result of an increase in the degree of crosslinking, as characterized by the gradual increase in both E' and E'' values in the rubbery state (values reported at 150 °C, from entries 3 to 5, Table 2). On the other hand, TGA traces of all the thin films derived from *st*-PVMA were rather similar, displaying similar decomposition profiles (Figure S10). Likewise, a thin film of *st*-PDAA was also solvent casted and subsequently photocured in the presence of 2 wt% of DMPA. The resulting material, *st*-PDAA-*hν*, exhibited a T_g of 56.1 °C as measured by DMA (Figure S11).

Figure 11. Photograph of solvent casted and photocured *st*-PVMA-*hν* film (0.06 mm thick).

Figure 12. Storage modulus (E' , top left), loss modulus (E'' , bottom left), and $\tan \delta$ (E''/E' , right) of *st*-PVMA (blue), photocured *st*-PVMA-*h* ν (purple), *st*-PVMA-*h* ν -SR3-2.5% (pink), *st*-PVMA-*h* ν -SR3-5% (red), and *st*-PVMA-*h* ν -SR3-10% (orange) determined by DMA analysis ($3\text{ }^{\circ}\text{C min}^{-1}$ temperature ramp rate).

Table 2. Selected thermo-mechanical properties of parent and photo-cured polymers characterized by DMA

entry no.	Polymer	T_g ($^{\circ}\text{C}$)	E' , 25 $^{\circ}\text{C}$ (GPa)	E'' , 25 $^{\circ}\text{C}$ (MPa)	E' , 150 $^{\circ}\text{C}$ (MPa)	E'' , 150 $^{\circ}\text{C}$ (MPa)
1	<i>st</i> -PVMA	105	1.64	171	1.16	0.22
2	<i>st</i> -PVMA- <i>h</i> ν	111	1.75	190	1.96	0.34
3	<i>st</i> -PVMA- <i>h</i> ν -SR3-2.5%	112	1.73	178	6.00	0.95
4	<i>st</i> -PVMA- <i>h</i> ν -SR3-5%	121	2.06	175	18.3	4.11
5	<i>st</i> -PVMA- <i>h</i> ν -SR3-10%	128	1.32	107	34.5	5.67
6	<i>st</i> -PDAA- <i>h</i> ν	56.1	1.04	90.7	49.8	5.47

Stereocomplexation and Photocuring to Robust Crosslinked Stereocomplexes.

Stereocomplexes of diastereomeric polymer chains were formed effectively by mixing 10 mg/mL acetone solutions of *it*-PMMA with *st*-PVMA (designated *sc*-PMMA-PVMA, Figure 1) or *it*-PMMA with *st*-PAMA (designated *sc*-PMMA-PAMA) at 40 $^{\circ}\text{C}$ in 1:1 and 1:2 *it*/*st*-polymer ratios, which were left to

slowly crystallize at room temperature to obtain colorless, transparent thin films. The formation of such stereocomplexes is readily evident by observing a characteristic T_m peak from the DSC curves (Figure 13 and Figure S12) and a characteristic diffraction peak at $2\theta = 4.56^\circ$ ($d = 1.94$ nm) from the pXRD patterns (Figure 14a).¹⁸ Interestingly, the T_m of the stereocomplexes was not significantly affected by the molar ratio of the diastereomeric polymer pair tested (1:1 vs. 1:2), but it is sensitive to the molecular weight of the *it*-PMMA component (Table 3). For instance, *sc*-PMMA-PVMA showed a T_m of 165 °C and 164 °C (in 1:1 and 1:2 ratios, respectively) with *it*-PMMA of $M_n = 26.4$ kg/mol ($D = 1.06$, $[mm] = 92.2$), while the same stereocomplex displayed a much higher T_m of 188 °C and 186 °C (in 1:1 and 1:2 ratios, respectively) with *it*-PMMA of much higher molecular weight ($M_n = 136$ kg/mol, $D = 1.19$, $[mm] = 96.4$). As expected, *it*-PAMA did not form a stereocomplex with either *st*-PAMA or *st*-PVMA in different ratios (1:1 and 1:2) and solvents (acetone and toluene) but, surprisingly, *it*-PAMA produced a weak stereocomplex with *st*-PMMA in both 1:1 and 1:2 ratios from their blends in acetone solutions, as revealed by broad T_m transitions of 119 °C (Figure 13 a) and 120 °C, respectively. To further examine the effects of the ester group in the isotactic polymer chain on the formation of stereocomplexes, we also attempted the stereocomplexation between isotactic poly(*n*-butyl methacrylate) ($[mm] = 96.9\%$, $M_n \sim 28$ kg/mol) and *st*-PVMA or *st*-PAMA in acetone (complexing solvent) in 1:1 and 1:2 *it/st* molar ratios. However, the resulting materials showed only two T_g 's corresponding to the constituent polymers, indicating that the stereocomplexation was hindered by the size of the *n*-butyl ester group of the isotactic polymer chain.

Control experiments by mixing *it*-PMMA with *st*-PVMA or *st*-PAMA in CH_2Cl_2 in a 1:1 *it/st* ratio led to amorphous polymer blends, which exhibited only the glass transitions corresponding to the constituent polymers of the blends, plus typical crosslinking exotherms of the vinyl-containing polymers appeared at temperatures higher than 150 °C. These results indicate that, just like *sc*-PMMA-PMMA, CH_2Cl_2 is also a non-complexing solvent for stereocomplexes *sc*-PMMA-PVMA and *sc*-PMMA-PAMA, the formation of which requires the use of complexing solvents such as acetone or toluene.

Figure 13. Representative DSC ($10\text{ }^{\circ}\text{C min}^{-1}$) curves: (a) *sc*-PAMA-PMMA (Table 3, entry 1); (b) *sc*-PMMA-PAMA (Table 3, entry 3); and (c) *sc*-PMMA-PVMA (Table 3, entry 11) obtained by crystallization from acetone solutions.

Figure 14. pXRD patterns of *sc*-PMMA-PVMA (a) and photocrosslinked *sc*-PMMA-PVMA-*hν* (b). Constituent diastereomeric polymers *st*-PVMA (c) and *it*-PMMA (d) included as a comparison.

Table 3. Stereocomplexation and photocrosslinking results ^a

entry no.	syndiotactic polymer	isotactic polymer	molar ratio (<i>st</i> / <i>it</i>)	<i>T</i> _m ^b (°C)	crosslinked vinyl polym. ^c (%)	trapped PMMA ^c (%)	PMMA trapping eff. ^c (%)
1	<i>st</i> -PMMA	<i>it</i> -PAMA	1:1	119	91.4	15.6	29
2	<i>st</i> -PAMA	—	—	—	97.2	—	—
3		low MW <i>it</i> -PMMA	1:1	155	77.7	12.5	23.0
4		low MW <i>it</i> -PMMA	2:1	157	85.8	20.0	29.9
5		high MW <i>it</i> -PMMA	1:1	165	85.5	51.8	73.4
6		high MW <i>it</i> -PMMA	2:1	168	84.7	50.5	67.2
7		(<i>it</i> -PMMA) _{0.83} - <i>b</i> -(<i>it</i> -PAMA) _{0.17}	1:1	168	63.7	49.1	86.7
8		(<i>it</i> -PMMA) _{0.67} - <i>b</i> -(<i>at</i> -PVMA) _{0.33}	1:1	170	79.0	63.0	89.6
9		(<i>it</i> -PMMA) _{0.88} - <i>ran</i> -(<i>it</i> -PAMA) _{0.12}	1:1	—	94.4	86.9	95.5
10	<i>st</i> -PVMA	—	—	—	58.3	—	—
11		low MW <i>it</i> -PMMA	1:1	165	56.5	56.2	99.6
12		low MW <i>it</i> -PMMA	2:1	164	56.2	13.5	31.4
13		high MW <i>it</i> -PMMA	1:1	188	62.7	50.5	88.6
14		high MW <i>it</i> -PMMA	2:1	186	54.1	39.0	78.7
15		(<i>it</i> -PMMA) _{0.83} - <i>b</i> -(<i>it</i> -PAMA) _{0.17}	1:1	181	66.4	58.5	93.9
16		(<i>it</i> -PMMA) _{0.67} - <i>b</i> -(<i>at</i> -PVMA) _{0.33}	1:1	182	71.1	59.8	92.6

^a Polymer data: *st*-PAMA, *M*_n = 39.9 kDa, *D* = 1.45, [*rr*] = 91.8; *it*-PAMA, *M*_n = 32.4 kDa, *D* = 1.10, [*mm*] = 96.5; *st*-PVMA, *M*_n = 52.1 kDa, *D* = 1.31, [*rr*] = 91.7; *st*-PMMA, *M*_n = 36.3 kDa, *D* = 1.29, [*rr*] = 93.7; low MW *it*-

PMMA, $M_n = 26.4$ kDa, $\bar{D} = 1.06$, $[mm] = 92.2$; high MW *it*-PMMA, $M_n = 136.1$ kDa, $\bar{D} = 1.19$, $[mm] = 96.4$; (*it*-PMMA)_{0.83}-*b*-(*it*-PAMA)_{0.17}, $M_n = 89.6$ kDa, $\bar{D} = 1.37$, $[mm] = 93.1\%$; (*it*-PMMA)_{0.67}-*b*-(*at*-PVMA)_{0.33}, $M_n = 76.8$ kDa, $\bar{D} = 1.49$, $[mm] = 79.8\%$, (*it*-PMMA)_{0.88}-*ran*-(*at*-PAMA)_{0.12}, $M_n = 156$ kDa, $\bar{D} = 1.83$, $[mm] = 95.9\%$. ^b T_m measured by DSC. ^c See the SI for the quantification method.

Under UV (350 nm) irradiation in the presence of photoradical initiator DMPA, the stereocomplex *sc*-PMMA-PVMA was successfully photocured into crosslinked, insoluble stereocomplex *sc*-PMMA-PVMA-*hν* (*c.f.*, Figure 1). The photocured stereocomplex exhibited a broad melting transition centered at ~150 °C (Figure S13), and a characteristic diffraction peak at $2\theta = 4.56$ °C ($d = 1.94$ nm) (Figure 14 b), thus confirming the stereocomplex structure is retained after crosslinking. Thin films of *sc*-PMMA-PVMA and photocrosslinked *sc*-PMMA-PVMA-*hν* were prepared and subsequently analyzed by DMA (Figure 15). While *it*-PMMA and *st*-PVMA showed a single sharp glass transition T_g at 45.2 °C and 105 °C, respectively, measured by the maxima of the $\tan \delta$ curve, the stereocomplex sample *sc*-PMMA-PVMA showed two weak transitions at higher temperatures of 62.2 °C and 135 °C. The photocrosslinked samples *sc*-PMMA-PVMA-*hν* exhibited a similar behavior with a shift of the transitions to even higher temperatures of 67.2 °C and 158 °C, attributable to the crosslinking of the polymer networks. Noteworthy also is that the stereocomplex exhibited considerably higher storage modulus than its constituent *it*-PMMA and *st*-PVMA at high temperatures and that the crosslinked stereocomplex had the highest modulus. For instance, at 95 °C, E' was measured to be 0.713, 43.8, 175, and 392 MPa for *it*-PMMA, *st*-PVMA, *sc*-PMMA-PVMA, and *sc*-PMMA-PVMA-*hν*, respectively. Overall, these thermo-mechanical and X-ray diffraction analysis results demonstrate that stereocomplex formation significantly increases storage and loss moduli over the constituent *it*- and *st*-polymers at temperatures > 100 °C and that the photocured stereocomplex retains the stereocomplex structure but with considerably enhanced thermal and mechanical properties of the material.

Figure 15. Storage modulus (E' , top left), loss modulus (E'' , bottom left), and $\tan \delta$ (E''/E' , right) of *it*-PMMA (red), *st*-PVMA (blue), *sc*-PMMA-PVMA (green), and *sc*-PMMA-PVMA-*hν* (purple) determined by DMA analysis ($3\text{ }^{\circ}\text{C min}^{-1}$ temperature ramp rate).

Besides the above demonstrated enhanced thermal and mechanical properties of the crosslinked stereocomplex, we anticipate another novel feature of the crosslinked stereocomplex: it should be solvent resistant and thus cannot be decomplexed in a non-complexing (or decomplexing) solvent such as chloroform, in contrast to the conventional *it*-PMMA/*st*-PMMA stereocomplex. To this end, we examined if the *it*-PMMA helical chains can be trapped inside the stereocomplex crosslinked via the outer helical layer of the vinyl-containing *st*-polymer. At the outset, a control experiment that consisted of a sample of *sc*-PMMA (a mixture of *it*-PMMA and *st*-PMMA in 1:1 ratio) containing 2 wt% of DMPA and subjected to UV irradiation ($\lambda = 350\text{ nm}$) for 2 h showed that the resulting stereocomplex was still completely soluble in chloroform and no PMMA was trapped due to no crosslinked chains. Using thermal crosslinking to trap the *it*-PMMA chains by annealing stereocomplex samples of *sc*-PMMA-PVMA and

sc-PMMA-PAMA over 200 °C, at which temperature thermal crosslinking occurs, was unsuccessful; while the *st*-polymer was successfully crosslinked at this temperature, the *it*-PMMA chains were released from the melt. Next, *sc*-PMMA-PVMA and *sc*-PMMA-PAMA were photocrosslinked with 2 wt% of DMPA under UV irradiation ($\lambda = 350$ nm) for 2 h at room temperature. The crosslinked material was extracted with chloroform (a decomplexing solvent) for 24 h at 40 °C to promote the possible release of the complexed, but untrapped, *it*-PMMA. The amount of the crosslinked *st*-polymer as well as the trapped *it*-PMMA was quantified by ^1H NMR analysis (see the SI). The *it*-PMMA trapping efficiency was calculated as the percentage of the experimental *it*-PMMA content (wt%) found vs the theoretical *it*-PMMA content in the crosslinked stereocomplex if all the initial *it*-PMMA was effectively trapped. Table 3 summarized our study of *it*-PMMA trapping efficiency as a function of (a) *it*-PMMA molecular weight; (b) molar ratio of *it*-PMMA to *st*-PVMA (or *st*-PAMA); and (c) use of block and random copolymers incorporating the photo-crosslinkable units.

The results summarized in Table 3 showed that a control sample of *st*-PAMA afforded a much higher degree of crosslinking (97.2%) compared to *st*-PVMA (58.3%) when photocured under the same conditions. Similarly, stereocomplexes containing both *it*-PAMA and *st*-PAMA samples were more effectively photocrosslinked (from 63.7% to 91.4% degree of crosslinking) than those containing *st*-PVMA (which achieved only 54.1% to 71.1%). Note that the self-crosslinking ability of *st*-PVMA in a sample crystallized from a CH_2Cl_2 solution (Table S1) was higher (82.4%), indicating that crystallization conditions impact the self-crosslinking ability of *st*-PVMA in the solid state. Under both conditions (acetone and CH_2Cl_2) tested, *st*-PAMA showed considerably better self-crosslinking ability (>95%) than *st*-PVMA, indicating that a longer, more flexible allyl ester group can be more efficiently crosslinked than the shorter and more rigid vinyl group in the VMA repeat unit. Stereocomplexes of *sc*-PMMA-PAMA with high MW *it*-PMMA ($M_n = 136.1$ kg/mol, $D = 1.19$) achieved a higher PMMA trapping efficiency (up to 73.4%, entry 5) than those stereocomplexes (up to 29.9, entry 4) with low MW *it*-PMMA ($M_n = 26.4$ kg/mol, $D = 1.06$). No correlation was observed between the PMMA trapping efficiency and the molar

ratio of the diastereomeric polymer pair. To possibly further enhance the PMMA trapping efficiency, we employed a new strategy of using block copolymers of *it*-PMMA with PAMA and PVMA to form stereocomplexes with *st*-PAMA and *st*-PVMA. Indeed, the PMMA trapping efficiency was enhanced to 86.7 and 89.6% (entries 7 and 8), indicating that a portion of the crosslinkable block is also photocured. The highest PMMA trapping efficiency of 95.5% (entry 9) was obtained from a blend of *st*-PAMA with a random copolymer, (*it*-PMMA)_{0.88}-*ran*-(*it*-PAMA)_{0.12}, but the stereocomplexation was hindered by the random placement of AMA units in the *it*-PMMA chain. In comparison, the PMMA trapping efficiency was generally higher (up to quantitative) for the stereocomplexes formed with *st*-PVMA (entries 11–16) than those with *st*-PAMA (entries 3–9). Again, higher PMMA trapping efficiencies were observed when block-copolymers containing crosslinkable AMA or VMA units were employed as the isotactic component to form the stereocomplex (> 92.6%, entries 15 and 16).

Additional control studies used the non-stereocomplexed control samples prepared by mixing *it*-PMMA with *st*-PVMA or *st*-PAMA in a non-complexing solvent (CH₂Cl₂), which were photocured under identical conditions to those reported for Table 3. The samples were further analyzed to quantify the capacity of the crosslinked *st*-vinyl polymers to trap *it*-PMMA and the results were summarized in Table S1. The results showed that the *it*-PMMA trapping efficiency was almost negligible (0.6 to 2.6%), indicating that the photocrosslinked polymer blends are not capable of trapping the *it*-PMMA chains. These control experiments highlight the importance of the polymer supramolecular structure to efficiently trap the *it*-PMMA chains, achievable only when the stereocomplexes are formed. For instance, while the *sc*-PMMA-PVMA formed in acetone had a PMMA trapping efficiency of 99.6% (entry 11, Table 3), the same mixture made in CH₂Cl₂ only showed a PMMA trapping efficiency of 2.6% (entry 4, Table S1).

We also investigated the possible complexation of *st*-PVMA and *st*-PAMA with fullerene C₆₀ to form an inclusion complex, *ic*-PVMA-C₆₀ or *ic*-PAMA-C₆₀. The material formed between *st*-PVMA and C₆₀ exhibited a broad melting transition peak at temperature > 150 °C, which was overlapped with much intense exothermic peaks (due to thermally induced crosslinking), thus offering no clear evidence for the

inclusion complex formation. However, we obtained conclusive evidence that *st*-PAMA readily forms inclusion complexes *ic*-PAMA-C₆₀ (Figure 16) with C₆₀ in different ratio combinations (Table 4). The formation of such inclusion complex was evidenced by the appearance of a sharp melting transition from 200 to 211 °C (Figure 17), observed from the DSC analysis of the resulting product after crystallization. The DSC thermograms of commercial fullerene C₆₀, *st*-PAMA, a non-inclusion mixture of *st*-PAMA/C₆₀ (obtained from the annealing of the blend at 80 °C for 20 h), and *ic*-PAMA-C₆₀ are shown in Figure 18 for comparison. The first-order transition in the DSC thermogram of C₆₀ corresponds to the well-known phase transition between a simple cubic (sc) lattice (below the $T_{tr} = -14.8$ °C) and a face-centered cubic lattice (fcc).³⁰ The *st*-PAMA shows a T_g of 49.9 °C, plus broad thermal crosslinking exothermic peak at temperature > 150 °C, whereas the non-inclusion complex mixture of *st*-PAMA/C₆₀ shows both mentioned features of the individual components. In sharp contrast, the *ic*-PAMA-C₆₀ obtained by crystallization from toluene exhibits a novel feature: a markedly sharp melting transition at $T_m = 205$ °C, indicative of the inclusion complex formation.

Three approaches were explored to produce crosslinked *ic*-PAMA-C₆₀. First, photochemically induced radical crosslinking with DMPA as the initiator under UV irradiation ($\lambda = 350$ nm) in solution or solid state did not produce the crosslinked product, as the crystallized material was again completely soluble in toluene. Second, thermally induced radical crosslinking with BPO (benzoyl peroxide) as the initiator also failed to afford the target crosslinked *ic*-PAMA-C₆₀. Third, recognizing C₆₀ as an excellent radical trap,³¹ we turned out attention to non-radical crosslinking methods. To this end, successful crosslinking of *ic*-PAMA-C₆₀ was achieved using 2 mol% of the Grubbs catalyst (2nd Gen.)³² in toluene at room temperature for 2 h (Figure 16; entries 3–5, Table 4). However, the DSC thermogram of the material obtained from the solution-phase metathesis crosslinking of *ic*-PAMA-C₆₀ exhibited no melting transition peak but a T_g of 106 °C, which is about 50 °C higher than the parent *st*-PAMA. This result indicates most, if not all, the helical inclusion complex structure was disrupted by this solution crosslinking reaction to form a mostly amorphous crosslinked structure (Figure 16).

Figure 16. Schematic representation of inclusion complex formation of *ic*-PAMA-C₆₀ and its crosslinking via olefin metathesis.

Table 4. Results of complexation between *st*-PAMA and C₆₀ and subsequent crosslinking by olefin metathesis ^a

entry no.	<i>st</i> -PAMA concentration (mg mL ⁻¹)	C ₆₀ solution (mg mL ⁻¹)	solvent	<i>T</i> _g ^b (°C)	<i>T</i> _m ^b (°C)	yield after crosslinking (%) ^c	encapsulated C ₆₀ content (wt%) ^d
1	5.0	1.0	Tol	47.9	200	n.d.	n.d.
2	5.0	2.0	Tol	53.1	206	n.d.	n.d.
3	10.0	1.0	Tol	53.6	207	>99	3.39
4	10.0	2.0	Tol	52.8	205	>99	4.77
5	10.0	10.0	Tol-DCB	56.3	207	>99	9.18
6	20.0	1.0	Tol	52.6	—	n.d.	n.d.
7	20.0	2.0	Tol	55.1	211	n.d.	n.d.
8	20.0	10.0	Tol-DCB	57.3	207	n.d.	n.d.

^a Conditions: 2.0 mL solvent (Tol = toluene or Tol-DCB = toluene/1,2-dichlorobenzene mixture in 50:50 vol%), except for entries 1 and 2 (5.0 mL); Grubbs' catalyst 2nd Gen. (2 mol%); *st*-PAMA (*M*_n = 39.9 kDa, *D* = 1.45, [*rr*] = 91.8); n.d. = not determined. ^b *T*_g and *T*_m before crosslinking measured by DSC. ^c Determined by gravimetric measurements. ^d Calculated by TGA.

Figure 17. DSC thermograms (10 °C min^{-1}) of *ic*-PAMA- C_{60} produced from toluene solutions of *st*-PAMA and C_{60} : Table 4, entry 1 (a), entry 3 (b), entry 4 (c), and entry 8 (d).

Figure 18. DSC (10 °C min^{-1}) thermograms of: commercial fullerene C_{60} powder (red); *st*-PAMA (blue); annealed blend of *st*-PAMA/ C_{60} at 80 °C for 20 h (black); and *ic*-PAMA- C_{60} from Table 4, entry 4 (purple).

Once successfully crosslinked, the C_{60} encapsulated inside the network of crosslinked *st*-PAMA- C_{60} cannot be reversibly recovered by dissolution of the inclusion complex as it is no longer soluble in toluene. A control reaction was performed to assess the Ru catalyst residue in the crosslinked complex by performing a crosslinking reaction of *st*-PAMA under the same conditions but without C_{60} . The content of C_{60} in the crosslinked complex was calculated through TGA analysis (Figure 19) by subtracting the residue in the trace at 500 °C of *st*-PAMA- C_{60} , minus the control experiment (3.49 wt%). These results indicated an uptake of C_{60} up to 9.18 wt% in the crosslinked *st*-PAMA- C_{60} when a 10.0 mg/mL solution of C_{60} in the feed was employed.

Figure 19. (a) TGA ($10\text{ }^{\circ}\text{C min}^{-1}$) traces of *st*-PAMA (black), crosslinked *st*-PAMA control (red), crosslinked *ic*-PAMA- C_{60} 3.43 wt% (orange), crosslinked *ic*-PAMA- C_{60} 4.77 wt% (green), and crosslinked *ic*-PAMA- C_{60} 9.18 wt% (purple); (b) microphotograph of *st*-PAMA film sample, and (c) microphotograph of crosslinked *ic*-PAMA- C_{60} 4.77 wt% film.

Conclusions

The perfectly chemoselective and highly syndiospecific coordination polymerization of divinyl polar monomers developed through this work has enabled the synthesis of highly syndiotactic polar vinyl polymers bearing the pendant reactive C=C bond on each repeat unit. Polymerization of three representative polar divinyl monomers (AMA, VMA, and DAA) by the C_s -ligated zirconocenium ester enolate catalysts under ambient conditions all achieved complete chemoselectivity and high stereoselectivity, producing the corresponding vinyl-functionalized polymers with syndiotacticity following this trend: *st*-PDAA (> 99% *rr*) > *st*-PVMA (96% *rr*) > *st*-PAMA (92% *rr*). Careful examination of the VMA polymerization by catalyst **5**, including synthetic, kinetic and mechanistic studies, showed that the polymerization follows a unimetallic, enantiomorphic-site controlled mechanism through the cationic cyclic metallacycle resting intermediate and exhibits the ability to control the resulting polymer M_n and $\bar{D}$ values. DFT calculations on free energy ΔG_{Stereo} of the transition state geometries for the competitive (correct and incorrect enantiofacial) additions in the polymerization of AMA and VMA provided a theoretical basis for the observed large difference in isotacticity of the polymers produced by C_2 -ligated catalyst **1**, but the rather similar syndiotacticity of the polymers produced by C_3 -ligated catalyst **5**.

The pendant vinyl groups of the obtained syndiotactic polymers can be completely converted into the corresponding thiolated polymers of the same tacticity, via the thiol-end click reaction with different thiols. Such polymers can also be readily photocured into flexible, crosslinked thin films for examining their thermo-mechanical properties, which revealed an expected increase in T_g , E' , and E'' values as the degree of crosslinking increases.

Vinyl-functionalized syndiotactic polymers, *st*-PVMA and *st*-PAMA, can readily form crystalline stereocomplexes with *it*-PMMA in a 2:1 or 1:1 molar ratio, but *st*-PVMA appears to form a stronger stereocomplex, as evidenced by the observed higher T_m , presumably due to the higher syndiotacticity of the constituent *st*-PVMA. Interestingly, *it*-PAMA also formed a weak stereocomplex with *st*-PMMA, and isotactic block copolymers *it*-PMMA-*b*-*it*-PAMA and *it*-PMMA-*b*-*it*-PVMA, but not their random

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2
3 copolymers, readily form crystalline stereocomplexes with either *st*-PAMA or *st*-PVMA; both findings
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5 extended the *it*-polymer capable of stereocomplexation beyond *it*-PMMA. The *it*-/*st*- stereocomplex, *sc*-
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7 PMMA-PVMA, can be readily photocured into a crosslinked, insoluble stereocomplex that exhibits high
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9 *it*-PMMA trapping efficiencies. Thermo-mechanical and X-ray diffraction analysis results showed that
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11 stereocomplex formation significantly increases storage and loss moduli over the constituent *it*- and *st*-
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13 polymers at temperatures > 100 °C and that the photocured stereocomplex retains the stereocomplex
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15 structure but with considerably enhanced thermal and mechanical properties of the material.
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19 *st*-PAMA readily forms inclusion complexes, *ic*-PAMA-C₆₀, with C₆₀ in different ratio
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21 combinations. Crosslinking of *ic*-PAMA-C₆₀ was achieved successfully *via* olefin metathesis using the
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23 Grubbs catalyst (2nd Gen.), while the photocuring in the presence of the photoinitiator was unsuccessful,
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25 attributable to C₆₀ being an excellent radical trap. The encapsulated C₆₀ in the resulting crosslinked *st*-
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27 PAMA-C₆₀ can no longer be released by dissolution of the inclusion complex, in contrast to the
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29 uncrosslinked inclusion complex.
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33 **Supplementary Information.** Full experimental details and additional figures (54 pages). This
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35 material is available free of charge on the ACS Publications website.
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