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Syringyl Methacrylate, a Hardwood Lignin-Based Monomer for High-T_g Polymeric Materials

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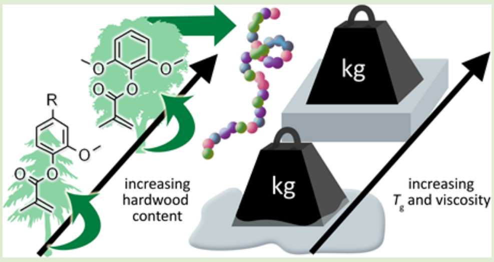
Supporting Information



ABSTRACT: As viable precursors to a diverse array of macromolecules, biomass-derived compounds must impart wide-ranging and precisely controllable properties to polymers. Herein, we report the synthesis and subsequent reversible addition−fragmentation chain-transfer polymerization of a new monomer, syringyl methacrylate (SM, 2,6-dimethoxyphenyl methacrylate), that can facilitate widespread property manipulations in macromolecules. Homopolymers and heteropolymers synthesized from SM and related monomers have broadly tunable and highly controllable glass transition temperatures ranging from 114 to 205 °C and zero-shear viscosities ranging from ∼0.2 kPa·s to ∼17,000 kPa·s at 220 °C, with consistent thermal stabilities. The tailorability of these properties is facilitated by the controlled polymerization kinetics of SM and the fact that one vs two *o*-methoxy groups negligibly affect monomer reactivity. Moreover, syringol, the precursor to SM, is an abundant component of depolymerized hardwood (e.g., oak) and graminaceous (e.g., switchgrass) lignins, making SM a potentially sustainable and low-cost candidate for tailoring macromolecular properties.

To address sustainability challenges associated with petrochemicals, researchers are exploiting a plethora of renewable chemicals to generate biobased, cost-effective, and thermomechanically useful macromolecules.[1−11] Lignin is one renewable resource that shows promise as a desirable alternative to petroleum feedstocks, largely due to its abundance as a byproduct of pulp and paper refining. Corresponding lignin-based bio-oils (e.g., the volatile fraction of pyrolyzed lignin) contain numerous aromatic compounds that structurally mimic common monomers (e.g., bisphenol A and styrene) for polymer applications.[4−7] The exact structure and composition of a lignin-based bio-oil is highly variable, depending on the biomass resource (tree, crop residue, grass, etc.), lignin type (Kraft, Organosolv, etc.), and depolymerization route (enzymatic, catalytic, etc.), among other factors.[12−17] In general, the native components of all lignin-based bio-oils include phenols and guaiacols (2-methoxyphenols), whereas the native components of angiosperm (hardwood—e.g., oak and maple tree) and graminaceous (grassy—e.g., switchgrass and corn stover) bio-oils also include syringols (2,6-dimethoxyphenols).[12−14]

Biobased compounds increasingly are being incorporated into thermoplastic elastomers (TPEs), pressure-sensitive adhesives, composite binders, and drug delivery vehicles,[7−11] all systems that benefit from macromolecules prepared via controlled polymerization techniques. The synthesis methods, such as reversible addition−fragmentation chain-transfer (RAFT), anionic, or atom-transfer radical polymerization,[18] are desirable for facilitating the generation of polymers (and block copolymers) with precise macromolecular characteristics through the control of kinetic parameters. For RAFT polymerizations, important parameters include the apparent propagation rate ($k_{p,app}$, which describes monomer-to-polymer conversion rates) and the apparent chain-transfer coefficient ($C_{tr,app}$, which describes the consumption rate of chain-transfer agent [CTA] and the conversion-dependent change in polymer dispersity [$Đ$]). Kinetic parameters that are consistent, in addition to controllable, also facilitate comparisons of polymer properties due to the ease with which macromolecules of matching end-groups, molecular weights, and $Đ$'s can be prepared.

For the above applications, properties that are among the most indicative of material practicality are the glass transition temperature (T_g) and the zero-shear viscosity (η_0). The T_g indicates the temperature at which a macromolecule transitions between glassy (solid-like) and rubbery (liquid-like) behavior, and the η_0 describes how easily a material may deform at a given temperature. Polymers with a T_g near 100 °C are useful for boiling-water-stable plastics, and polymers with a T_g well above 100 °C are useful for high-temperature applications (e.g., machine parts and asphalt components). Ideally, one could access T_g's anywhere from 100 to 200 °C via biobased monomers and controlled polymerizations; however, a dearth of examples is noted for high molecular weight macromolecules

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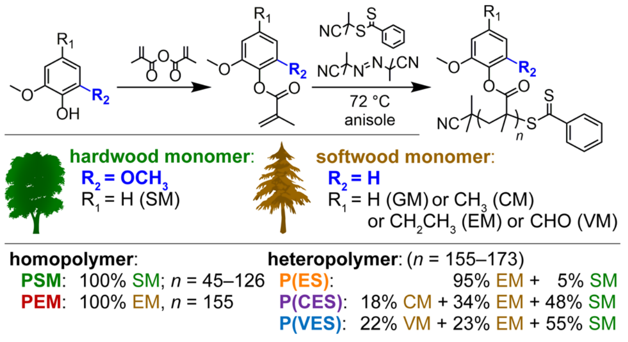
with T_g's in the range of ≈135−190 °C,[7] although some polymers come close.[11,19,20] Furthermore, materials with η_0's of ∼10−100 Pa·s (e.g., condiments) are easily spread and shaped, and those with η_0's of ∼10^6−10^8 Pa·s (e.g., bitumen for roads) are highly deformation resistant. An ability to choose between these T_g's and η_0's in a biobased macromolecule would be ideal for optimizing processability and mechanical strength in the pursuit of sustainable macromolecules prepared using controlled means.

The major lignin-based bio-oil components that have been incorporated into controlled polymerizations are guaiacols with varying *p*-position R-groups, as shown in Scheme 1.[21−23] The different functionalities (e.g., ethyl, methyl, formyl, and hydrogen R-groups) are seen as potential handles for modulating polymer properties,[21−23] but the resulting macromolecules have a fairly narrow range of accessible properties. Specifically, poly(4-ethylguaiacyl methacrylate) (PEM) has the lowest T_g of ≈110 °C and η_0 of 7 × 10^5 Pa·s at 150 °C, while poly(vanillin methacrylate) (PVM) has the highest T_g of ≈130 °C and η_0 of 3 × 10^7 Pa·s at 150 °C.[23] Although this range is useful for the fine-tuning of macromolecular properties, it does not lead to ultimate material versatility.[23]

Scheme 1. Synthesis Scheme, Nomenclature, Mass Compositions, and Degrees of Polymerization (*n*'s) of Lignin-Based Monomers and Polymers Reported Herein



Herein, a syringol derivative, syringyl methacrylate (SM), is synthesized for the first time and incorporated into controlled polymerizations to greatly expand the window of T_g's and η_0's accessible via biobased monomers. In fact, as shown below, the T_g for PSM is greater than that reported for almost any other amorphous polymer lacking cyclic groups in the backbone, yet the monomer is readily polymerizable, especially in comparison to other high-T_g phenyl methacrylates, such as 2,6-dimethylphenyl methacrylate. An additional advantage of the syringols in comparison to the guaiacols is the potential abundance of the former; syringols constitute anywhere from ∼40 wt % to 90 wt % of identified monophenolic compounds in fractions of thermally decomposed hardwood or grassy lignins,[12] and ∼60 wt % of pulpwood worldwide comes from hardwood trees that contain syringylic components.[24] These characteristics make syringols ideal biobased precursors to polymers.

Furthermore, heteropolymers (multicomponent polymers) containing SM segments are prepared in this study to show that properties of macromolecules can be widely manipulated via SM content, while also enabling greater usage of bio-oil fractions, consistent with biobased materials objectives.[11,22,23,25−27] To this end, SM was incorporated into polymerizations of mixed softwood lignin-based monomers, viz., EM, VM, and creosyl methacrylate (CM), in which these components, the corresponding heteropolymers, and the macromolecules' weight compositions are shown in Scheme 1. Poly(CM-*co*-EM-*co*-SM) [P(CES)] and poly(VM-*co*-EM-*co*-SM) [P(VES)] have compositions that approximately mimic the compositions reported for a bio-oil prepared from switchgrass Organosolv lignin[12] [weight-fraction SM (f_S) = 0.48 for P(CES) and 0.55 for P(VES)], and poly(EM-*co*-SM) [P(ES), f_S = 0.05] has a composition that was chosen to show that small amounts of SM can be incorporated into a polymer and measurably change its properties.

SM, PSM, and SM-containing heteropolymers were synthesized successfully by employing procedures akin to those used for softwood lignin-based monomers and polymers[28] (see Scheme 1 and also the Supporting Information). The successful synthesis and isolation of SM was somewhat unexpected, mainly because syringol tends to favor conversion to stable phenoxy radicals and colored quinones.[29,30] The success of the SM RAFT polymerizations also was somewhat unexpected due to the *o*-methoxy groups; namely, other poly(phenyl methacrylate) derivatives with bulky *o*-groups can be challenging to synthesize due to low ceiling temperatures and polymer thermal stabilities.[31,32]

The polymerization rate and reactivity of SM are consistent with the polymerization rate and reactivity of softwood monomers (EM, CM, VM, and guaiacyl methacrylate [GM]),[22] despite the hardwood monomer's second *o*-position methoxy group. The $k_{p,app}$'s, which are illustrated by the lines in Figure 1a for polymerizations performed under approximately identical reaction conditions, are the same at 95% confidence regardless of SM content and compare favorably to the $k_{p,app}$'s previously reported for softwood monomers[22] ($k_{p,app}$ = 0.25 ± 0.01 h^{-1} for PSM-24[33] and 0.23−0.26 h^{-1} for SM-containing heteropolymers, vs 0.21−0.29 h^{-1} for guaiacylic polymers;[22] exact values are listed in Table S2). The compositions of the monomer mixtures and the cumulative compositions of the heteropolymer chains also do not change measurably with respect to conversion [*x*] (see Figure S1), further indicating the similar reactivities of the hardwood and softwood monomers and the likely random distributions of monomer segments in each chain. Consequently, syringol and guaiacol contents in a mixture can be manipulated without harming the predictability of conversions, monomer distributions, and molecular weight.

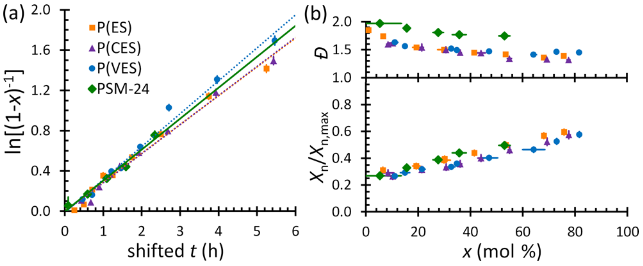


Figure 1. (a) Pseudo-first-order kinetic data, in which *x* is molar percent conversion and *t* is reaction time shifted by 0.02−0.24 h to a pre-equilibrium time of 0 h. The lines are the linearized fits used to estimate $k_{p,app}$ [lines for P(ES) and P(CES) are indistinguishable]. (b) Conversion-dependent molecular weight characteristics (Đ and normalized degree of polymerization, $X_n/X_{n,max}$) of polymers containing SM units. These data indicate the consistent RAFT polymerization characteristics of lignin-based polymers regardless of SM content.

Control over the RAFT polymerizations also is consistent between guaiacylic[22] and syringylic monomers, simplifying the process of tailoring macromolecular characteristics. First, as shown by the data in Figure 1b, the *Đ*'s decrease with respect to increasing x, and the normalized degrees of polymerization ($X_n/X_{n,max}$'s) change linearly with x, indicating that the polymerizations are controlled. Second, the size-exclusion chromatography (SEC) data are unimodal (see Figure S2), and the *Đ*'s of the homopolymers and heteropolymers (1.32–1.74, see Table S1) are similar to or better than what was reported for PVMs that were successfully chain-extended to generate self-assembling block copolymers.[21] Finally, the *Đ*'s and $X_n/X_{n,max}$'s for the homopolymers and heteropolymers change with respect to x in an approximately equivalent manner, albeit slightly shifted vertically due to differences in polymer solubility. The consistency of these data was confirmed by estimating the $C_{tr,app}$ from the heteropolymerizations using the Mayo equation.[22] The resulting $C_{tr,app}$'s for the heteropolymers were within error of values reported for the polymerizations of GM, EM, CM, VM, and corresponding mixtures ($C_{tr,app}$ = 1.4–2.8 for softwood monomers and mixtures[22] vs 2.3–3.0 for SM-containing mixtures, as listed in Table S2). Additionally, $C_{tr,app}$ for SM homopolymerizations is approximately the same as for softwood monomer polymerizations,[34] further supporting that the second *o*-methoxy group has a negligible effect on the polymerization behavior of lignin-based methacrylates.

PSM-24 has a high *Đ* in part because the reaction mixture gelled. Lower *Đ*'s listed in Table S1 have been achieved by diluting the reaction, reducing the target molecular weight, changing the solvent, and incorporating softwood lignin-based methacrylate monomers. All of these changes contribute to reductions in solution viscosity and thus *Đ*.[35,36]

The measured T_g's of the PSM homopolymers (185–205 °C depending on molecular weight, see also Table S1) are among the highest reported for amorphous, linear polymers with aliphatic backbones, even greater than the T_g's reported for poly(2,6-dimethylphenyl methacrylate) (189 °C) and poly(2,6-diisopropylphenyl methacrylate) (198 °C).[37] A PSM of infinite molecular weight could have a T_g as high as ≈220 °C, assuming Flory–Fox behavior when fitting data from Table S1. The T_g of PSM-24 is ≈75 °C higher than that of PVM and ≈95 °C higher than that of PEM at similar number-average molecular weight. The differential scanning calorimetry (DSC) data for PEM and SM-containing polymers are shown in Figure 2 for comparison.

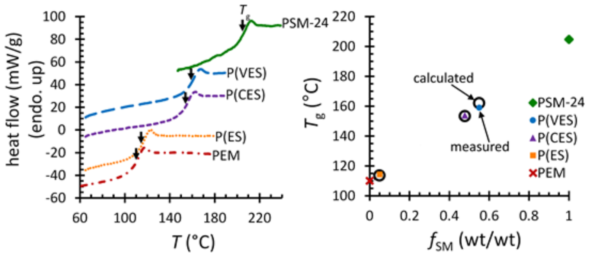


Figure 2. DSC data and the corresponding measured and calculated (via the Fox equation) T_g's as a function of SM-content, which together show the wide-ranging and predictable T_g's available through hardwood and softwood lignin-based methacrylates. DSC data were shifted vertically and normalized to a slope of zero at $T > T_g$ for clarity. PEM data were reported previously.[23]

SM segments also can be incorporated into polymers to make predictable changes to the T_g based on composition and the Fox equation.[38] The actual and calculated Fox-based T_g's agree closely, as shown in Figure 2, in which the black circles (calculated T_g's) overlay the colored shapes (measured T_g's). For example, incorporating 5 wt % of SM segments into PEM raises the T_g by 4 °C (from 110 to 114 °C), the predicted increase. The heteropolymers with compositions that mimic possible fractions of bio-oil (f_{SM} = 0.48–0.55) have similarly predictable, yet high (154 and 159 °C) T_g's. Furthermore, the onset thermal degradation temperatures in air (see Table S2 and Figure S3) for PSM (303 ± 5 °C) and the heteropolymers (256–260 °C) are ≈100 °C greater than each of the measured T_g's; thus, these polymers can be melt processed without significant thermal degradation.

The high T_g of PSM and its effectiveness for tailoring polymer T_g's results more from differences in monomer structure than tacticity. PSM is somewhat more syndiotactic than the softwood lignin-based polymers (see Supporting Information for racemo diad and syndiotactic triad contents), yet the T_g differential between the hardwood and softwood monomers is far more significant than the differences reported for other atactic vs syndiotactic vs isotactic methacrylate polymers. The T_g increase between atactic and syndiotactic poly(methyl methacrylate) is 10 °C,[39] and the T_g difference between isotactic and syndiotactic poly(phenyl methacrylate)s and poly(4-methoxyphenyl methacrylate)s is similarly small.[40] Instead, the factor contributing most significantly to the T_g likely is the restricted rotational freedom of the side chain around the phenol–ester linkage, which arises from interactions between the carbonyl in the ester and bulky *o*-groups. This explanation is consistent with the rigidity argument previously applied to explain T_g differences between poly(phenyl methacrylates) with varying *o*-alkyl substituents.[37,41]

The η_0's for SM-containing polymers span ~5 orders of magnitude and depend largely on the SM content. This promising range of deformation resistances accessible via lignin-based monomers is illustrated in Figure 3a (see also Figures S4 and S5 for related dynamic mechanical analysis data). For example, the η_0 at 220 °C is 17,000 kPa·s for PSM and significantly less for the SM-containing heteropolymers (0.2–40 kPa·s), as shown in Figure 3b and listed in Table S2. This window of η_0's is substantial in comparison to the ~2 orders of magnitude spanned by the complete range of guaiacylic methacrylate polymers[23] and could be wider if higher molecular weight polymers, relative to PSM-24, were examined. Thus, SM provides a much wider space over which processability and deformation resistance can be optimized.

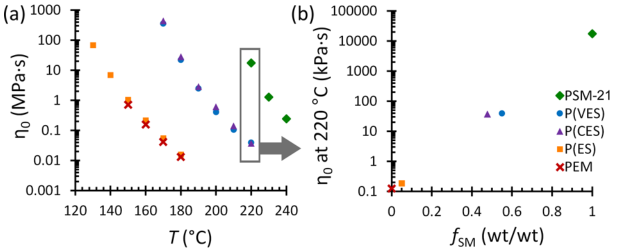


Figure 3. Zero-shear viscosities (a) as a function of temperature and (b) as a function of SM content, which together show the wide-ranging η_0's available through hardwood and softwood LBMs. Data for PEM were reported previously.[23]

In summary, no other system of biobased monomers allows T_g's from ≈100 °C (ideal for thermoformable yet boiling-water-stable plastics, such as cups) to ≈200 °C (ideal for heat- and flow-resistant materials, such as asphalt binders) to be accessed as readily as the lignin-based monomers presented herein. The measurable changes in T_g and η_0 at small SM contents, and the wide-ranging thermomechanical properties reported for all of these polymers, indicate that SM could be a powerful add-in monomer for adjusting material properties. The similar polymerization characteristics between softwood and hardwood monomers also greatly simplify the task of predicting *a priori* macromolecular characteristics and properties of any heteropolymer containing syringylic segments. Hence, SM is an extraordinary new biobased monomer for its ability to significantly raise polymer T_g's and deformation resistances at small added contents, so the isolation of syringol from hardwood or grassy lignin-based bio-oils and its conversion to SM has the potential to become a worthwhile investment.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.6b00270.

> Experimental conditions and methods, macromolecular characteristics, table of heteropolymer properties, SEC data, composition vs conversion data, thermolysis data, and additional rheology data (PDF)

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Notes

The authors declare no competing financial interest.

‖Deceased: 24 March 2015

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■ REFERENCES

(1) Mathers, R. T. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50* (1), 1–15.

(2) Mülhaupt, R. *Macromol. Chem. Phys.* **2013**, *214* (2), 159–174.

(3) Isikgor, F. H.; Becer, C. R. *Polym. Chem.* **2015**, *6* (25), 4497–4559.

(4) Llevot, A.; Grau, E.; Carlotti, S.; Grelier, S.; Cramail, H. *Macromol. Rapid Commun.* **2016**, *37* (1), 9–28.

(5) Delidovich, I.; Hausoul, P. J. C.; Deng, L.; Pfützenreuter, R.; Rose, M.; Palkovits, R. *Chem. Rev.* **2015**, *116*, 1540.

(6) Gandini, A.; Lacerda, T. M. *Prog. Polym. Sci.* **2015**, *48*, 1–39.

(7) Holmberg, A. L.; Reno, K. H.; Wool, R. P.; Epps, T. H., III *Soft Matter* **2014**, *10* (38), 7405–7424.

(8) Yao, K.; Tang, C. *Macromolecules* **2013**, *46* (5), 1689–1712.

(9) Satoh, K. *Polym. J.* **2015**, *47* (8), 527–536.

(10) Hillmyer, M. A.; Tolman, W. B. *Acc. Chem. Res.* **2014**, *47* (8), 2390–2396.

(11) Gallagher, J. J.; Hillmyer, M. A.; Reineke, T. M. *ACS Sustainable Chem. Eng.* **2015**, *3* (4), 662–667.

(12) Kim, J.-Y.; Park, J.; Hwang, H.; Kim, J. K.; Song, I. K.; Choi, J. W. *J. Anal. Appl. Pyrolysis* **2015**, *113*, 99–106.

(13) Asmadi, M.; Kawamoto, H.; Saka, S. *J. Anal. Appl. Pyrolysis* **2011**, *92* (2), 417–425.

(14) Buranov, A. U.; Mazza, G. *Ind. Crops Prod.* **2008**, *28* (3), 237–259.

(15) Ragauskas, A. J.; Beckham, G. T.; Biddy, M. J.; Chandra, R.; Chen, F.; Davis, M. F.; Davison, B. H.; Dixon, R. A.; Gilna, P.; Keller, M.; Langan, P.; Naskar, A. K.; Saddler, J. N.; Tschaplinski, T. J.; Tuskan, G. A.; Wyman, C. E. *Science* **2014**, *344* (6185), 1246843.

(16) Kanaujia, P. K.; Sharma, Y. K.; Garg, M. O.; Tripathi, D.; Singh, R. *J. Anal. Appl. Pyrolysis* **2014**, *105*, 55–74.

(17) Xu, C.; Arancon, R. A. D.; Labidi, J.; Luque, R. *Chem. Soc. Rev.* **2014**, *43* (22), 7485–7500.

(18) Bates, F. S.; Hillmyer, M. A.; Lodge, T. P.; Bates, C. M.; Delaney, K. T.; Fredrickson, G. H. *Science* **2012**, *336* (6080), 434–440.

(19) Mosnáček, J.; Matyjaszewski, K. *Macromolecules* **2008**, *41* (15), 5509–5511.

(20) Shin, J.; Lee, Y.; Tolman, W. B.; Hillmyer, M. A. *Biomacromolecules* **2012**, *13* (11), 3833–3840.

(21) Holmberg, A. L.; Stanzione, J. F., III; Wool, R. P.; Epps, T. H., III *ACS Sustainable Chem. Eng.* **2014**, *2* (4), 569–573.

(22) Holmberg, A. L.; Karavolias, M. G.; Epps, T. H., III *Polym. Chem.* **2015**, *6* (31), 5728–5739.

(23) Holmberg, A. L.; Nguyen, N. A.; Karavolias, M. G.; Reno, K. H.; Wool, R. P.; Epps, T. H., III *Macromolecules* **2016**, *49* (4), 1286–1295.

(24) FAO *Yearbook of Forest Products 2013*; Food and Agriculture Organization of the United Nations: Rome, Italy, 2015; pp 54–55.

(25) Fache, M.; Boutevin, B.; Caillol, S. *Green Chem.* **2016**, *18* (3), 712–725.

(26) Stanzione, J. F., III; Giangiulio, P. A.; Sadler, J. M.; La Scala, J. J.; Wool, R. P. *ACS Sustainable Chem. Eng.* **2013**, *1* (4), 419–426.

(27) Wang, S.; Vajjala Kesava, S.; Gomez, E. D.; Robertson, M. L. *Macromolecules* **2013**, *46* (18), 7202–7212.

(28) Stanzione, J. F., III; Sadler, J. M.; La Scala, J. J.; Wool, R. P. *ChemSusChem* **2012**, *5* (7), 1291–1297.

(29) Steelink, C. *J. Am. Chem. Soc.* **1965**, *87* (9), 2056–2057.

(30) Altwicker, E. R. *Chem. Rev.* **1967**, *67* (5), 475–531.

(31) Otsu, T.; Yamada, B.; Sugiyama, S.; Mori, S. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18* (7), 2197–2207.

(32) Yamada, B.; Sugiyama, S.; Mori, S.; Otsu, T. *J. Macromol. Sci., Chem.* **1981**, *15* (2), 339–345.

(33) The hyphenated value following a homopolymer designation corresponds to that material's number-average molecular weight listed in Table S1.

(34) A similar evaluation of $C_{tr,app}$ was not made for PSM due to the unsuitability of comparing $Đ$ data taken using different instrumentation and solvents. In this case, SEC data for PSM were collected in chloroform instead of tetrahydrofuran (the eluent for the other polymers) due to solubility issues.

(35) Trommsdorff, V. E.; Köhle, H.; Lagally, P. *Makromol. Chem.* **1948**, *1* (3), 169–198.

(36) Norrish, R. G. W.; Smith, R. R. *Nature* **1942**, *150*, 336–337.

(37) Gargallo, L.; Hamidi, N.; Radić, D. *Thermochim. Acta* **1987**, *114* (2), 319−328.

(38) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.

(39) O'Reilly, J. M.; Bair, H. E.; Karasz, F. E. *Macromolecules* **1982**, *15* (4), 1083−1088.

(40) Wesslén, B.; Gunneby, G.; Hellström, G.; Svedling, P. *J. Polym. Sci., Polym. Symp.* **1973**, *42* (1), 457−465.

(41) Gargallo, L.; Hamidi, N.; Radić, D. *Polymer* **1990**, *31* (5), 924−927.