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Thermodynamic Interactions between Polystyrene and Long-Chain Poly(*n*-Alkyl Acrylates) Derived from Plant Oils

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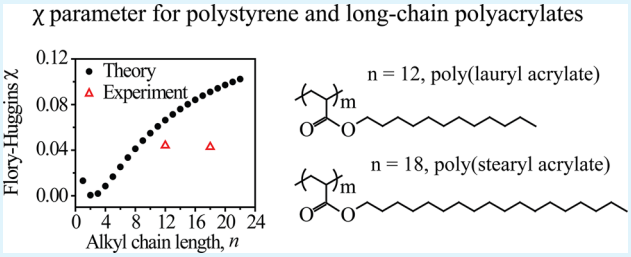
Supporting Information

ABSTRACT: Vegetable oils and their fatty acids are promising sources for the derivation of polymers. Long-chain poly(*n*-alkyl acrylates) and poly(*n*-alkyl methacrylates) are readily derived from fatty acids through conversion of the carboxylic acid end-group to an acrylate or methacrylate group. The resulting polymers contain long alkyl side-chains with around 10−22 carbon atoms. Regardless of the monomer source, the presence of alkyl side-chains in poly(*n*-alkyl acrylates) and poly(*n*-alkyl methacrylates) provides a convenient mechanism for tuning their physical properties. The development of structured multicomponent materials, including block copolymers and blends, containing poly(*n*-alkyl acrylates) and poly(*n*-alkyl methacrylates) requires knowledge of the thermodynamic interactions governing their self-assembly, typically described by the Flory−Huggins interaction parameter χ. We have investigated the χ parameter between polystyrene and long-chain poly(*n*-alkyl acrylate) homopolymers and copolymers: specifically we have included poly(stearyl acrylate), poly(lauryl acrylate), and their random copolymers. Lauryl and stearyl acrylate were chosen as model alkyl acrylates derived from vegetable oils and have alkyl side-chain lengths of 12 and 18 carbon atoms, respectively. Polystyrene is included in this study as a model petroleum-sourced polymer, which has wide applicability in commercially relevant multicomponent polymeric materials. Two independent methods were employed to measure the χ parameter: cloud point measurements on binary blends and characterization of the order−disorder transition of triblock copolymers, which were in relatively good agreement with one another. The χ parameter was found to be independent of the alkyl side-chain length (n) for large values of n (i.e., $n > 10$). This behavior is in stark contrast to the n-dependence of the χ parameter predicted from solubility parameter theory. Our study complements prior work investigating the interactions between polystyrene and short-chain polyacrylates ($n \leq 10$). To our knowledge, this is the first study to explore the thermodynamic interactions between polystyrene and long-chain poly(*n*-alkyl acrylates) with $n > 10$. This work lays the groundwork for the development of multicomponent structured systems (i.e., blends and copolymers) in this class of sustainable materials.



KEYWORDS: *renewable resource polymers, poly(n-alkyl acrylates), poly(n-alkyl methacrylates), Flory−Huggins interaction parameter, alkyl chain length, side-chain, block copolymers, thermodynamic interactions*

INTRODUCTION

Vegetable oils and their fatty acids are promising replacements for petroleum sources for the derivation of polymers because of their abundance, low cost, lack of toxicity, biodegradability, and ease of functionalization that provides convenient routes to polymerization.[1] In one synthetic procedure, the carboxylic acid end-group of a fatty acid is converted to a hydroxyl group[2] and subsequently converted to an acrylate or methacrylate group, forming a long-chain *n*-alkyl acrylate or *n*-alkyl methacrylate.[3] Long-chain *n*-alkyl acrylates and *n*-alkyl methacrylates can be readily polymerized through free radical[4−6] or controlled radical[7−10] techniques to form poly(*n*-alkyl acrylates) and poly(*n*-alkyl methacrylates). When derived from fatty acids, the poly(*n*-alkyl acrylates) and poly(*n*-alkyl methacrylates) contain alkyl side-chains of length ranging between 10 and 22 carbon atoms, depending on the choice of fatty acid.[1]

Whether derived from plant or petroleum sources, the presence of side-chains in poly(*n*-alkyl acrylates) and poly(*n*-alkyl methacrylates) provides a convenient mechanism for tuning their physical properties. Previous studies by others have shown that the melting temperature, heat of fusion, crystallite size, gas permeability, and ultrasonic degradation rate of homopolymers and copolymers composed of poly(*n*-alkyl acrylates) and poly(*n*-alkyl methacrylates) are dependent on the alkyl side-chain length.[4,11−17] Our group has recently demonstrated that the melt viscosity of copolymers composed of long-chain poly(*n*-alkyl acrylates) is also dependent on the side-chain length.[18] Long-chain poly(*n*-alkyl acrylates) and poly(*n*-alkyl methacrylates) have been incorporated in a variety

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of classes of polymeric materials, including block copolymers,[7,9,18−25] thermoplastic elastomers,[18,19] pressure sensitive adhesives,[26,27] brushes,[28] and shape memory materials.[29]

The development of structured multicomponent materials, including block copolymers and blends, requires knowledge of the thermodynamic interactions governing their self-assembly. In this work, we focus on blends and block copolymers which contain long-chain poly(*n*-alkyl acrylates) and polystyrene. Polystyrene is chosen as a model component of these blends and copolymers to probe the impact of the length of the side-chain in the long-chain poly(*n*-alkyl acrylates) on the thermodynamic interactions between the material components. Polystyrene is a highly relevant petroleum-sourced polymer, employed in diverse multicomponent materials that contain polyolefins, polydienes, polyacrylates, and polymethacrylates, among others, making it an ideal candidate for fundamental studies on blend thermodynamics. The Flory−Huggins interaction parameter, χ, (or the related binary interaction energy density) is traditionally employed to characterize the thermodynamic interactions between polymers.[30,31] The length of the side-chain of short-chain poly(*n*-alkyl acrylates) and poly(*n*-alkyl methacrylates) has been demonstrated to greatly influence their interactions with other polymers. Previous studies have characterized the χ parameter between polystyrene and various short-chain poly(*n*-alkyl acrylates) using a variety of experimental techniques: cloud-point measurements or miscibility studies of blends,[32,33] the domain spacing of block copolymer melts,[34] melt titration,[35] and swelling experiments on interpenetrating networks.[36,37] A wider body of literature exists for the measurement of the χ parameter between polystyrene and various short-chain poly(*n*-alkyl methacrylates), particularly for mixtures of polystyrene and poly(methyl methacrylate), employing cloud-point measurements or miscibility studies of blends,[33,38−45] small-angle neutron scattering,[46−49] neutron reflectivity,[49,50] solution behavior,[51−53] PVT experiments,[40] melt titration,[35] and swelling experiments on cross-linked polymers.[54] Furthermore, molecular dynamics simulations have been employed.[55,56]

Few studies have directly examined the influence of the side-chain length on the thermodynamic interactions between polystyrene and poly(*n*-alkyl acrylates) or poly(*n*-alkyl methacrylates), especially for large *n*. Two key studies have demonstrated that the solubility parameter of poly(*n*-alkyl acrylates) and poly(*n*-alkyl methacrylates) decreases with increasing alkyl chain length (*n*) for relatively short side-chain lengths (up to $n = 10$).[32,57] Systematic experimental measurements of the binary interaction energy density (which is directly related to the χ parameter) with increasing *n* were not in agreement with that predicted from the solubility parameters.[32] Importantly, experimental measurements indicated that the binary interaction energy density increases only slightly when *n* increases from $n = 4$ to 10, in stark disagreement with the predictions from the solubility parameters.[32] To our knowledge, no previous studies have examined the thermodynamic interactions between polystyrene and long-chain poly(*n*-alkyl acrylates) or poly(*n*-alkyl methacrylates) (i.e., when *n* is greater than 10).

The objective of this work is to probe the influence of the alkyl side-chain length on the χ parameter in the regime of long side-chain lengths (i.e., $n > 10$). Our model system contains polystyrene and long-chain poly(*n*-alkyl acrylate) homopolymers and copolymers: specifically, we have included poly(stearyl acrylate), poly(lauryl acrylate), and their random copolymers. Lauryl and stearyl acrylate are derived from vegetable oils such as soybean, linseed, coconut, and palm kernel oils. For poly(lauryl acrylate) and poly(stearyl acrylate), the alkyl chain length, *n*, is 12 and 18, respectively. We have employed two experimental methods of characterizing the χ parameter: cloud point measurements on binary blends and determination of the order−disorder transition temperature of triblock copolymers. The values of $\chi(T)$ determined from both methods are compared, and the alkyl side-chain length-dependence of the χ parameter is examined.

EXPERIMENTAL METHODS

Materials. All chemicals were purchased from Sigma-Aldrich unless otherwise noted below.

Polymer Synthesis and Characterization. Polystyrene (PS), poly(lauryl acrylate) [PLAc], poly(stearyl acrylate) [PSAc], poly(lauryl acrylate-*co*-stearyl acrylate) [poly(LAc-*co*-SAc)] random copolymers, and poly(styrene-*b*-(LAc-*co*-SAc)-*b*-styrene) (SAS) triblock copolymers were synthesized with reversible addition−fragmentation chain transfer polymerization, following procedures described in ref 18.

Molecular weight and molecular weight distribution (the dispersity, *Đ*) were characterized by a Viscotek gel permeation chromatography (GPC) instrument with Agilent ResiPore columns, using THF (OmniSolv, HPLC grade) as the mobile phase at 30 °C. The flow rate was 1 mL/min and the injection volume was 100 μL. A triple detection system, including light scattering, a viscometer and refractometer, was employed to characterize the absolute molecular weight. Representative GPC chromatographs for the polymers used in this study are included in the Supporting Information (Figures S1−S4).

Proton nuclear magnetic resonance (^{1}H NMR) experiments were performed on a JEOL ECA-500 instrument using deuterated chloroform (99.8 atom % D) as the solvent. ^{1}H NMR was utilized to determine the composition of the polyacrylate random copolymers and triblock copolymers (procedures are provided in ref 18). ^{1}H NMR was also used to characterize the relative proportions of meso and racemo dyads in the PLAc and PSAc homopolymers (evaluated following methods reported in refs,[8,58] and summarized in Figure S5 and Table S1 in the Supporting Information). PLAc and PSAc contained 39 and 36% meso dyads, respectively.

Flory−Huggins Interaction Parameter. Two methods were employed to characterize the Flory−Huggins interaction parameter (χ) between polystyrene and the polyacrylates: cloud point measurements and rheology.

Cloud Point Measurements. Films consisting of PS/PLAc (or PS/PSAc) blends were cast from dichloromethane solutions at room temperature on microscope slides. The films were allowed to air-dry and were subsequently dried in a vacuum oven at 150 °C for 4 h. The sample was covered by a second slide and sealed using 3M Scotch-Weld Epoxy Adhesive to avoid the thermal degradation of the polymers at elevated temperatures. The cloud point temperatures were determined through observing the optical character of the sample in a microscope (Olympus BX51TRF) equipped with a heating cell (Instec HCS302-01). The sample temperature was first calibrated with a thermocouple and a calibration curve was constructed relating the sample temperature to the reported heating cell temperature. The sample was first heated to a temperature at which the blend was transparent, indicating the two polymers were miscible, and the sample was then cooled down slowly by 1 °C increment, and stabilized at each temperature for 2 min before observation of the sample with the microscope. The temperature at which the sample started to become opaque was identified as the cloud point temperature. The accuracy of the cloud point temperature is estimated to be within ±1 °C for all experiments based on repeat measurements of the same sample. Experiments conducted upon heating to identify the location of the phase boundary were consistent with the results obtained upon cooling (observed difference was ≤2 °C).

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Rheology. The order−disorder transition temperatures (T_{ODT}) of SAS triblock copolymers were probed using a TA Instruments DHR-2 rheometer. A polymer disk with 25 mm diameter and 1 mm thickness was prepared by compression molding on a Carver Hotpress at an applied load of 4000 lbs at 210 °C. After cooling down to room temperature, the polymer disk was loaded between two 25 mm electrically heated parallel plates with a gap of around 1 mm. Nitrogen flowed continuously through the sample environment to avoid degradation of the polymer. The linear viscoelastic region was first determined using a strain sweep (1−50% strain) at a frequency of 10 rad/s. A frequency sweep was then completed (1−50 rad/s) using a strain in the linear region. This procedure was repeated upon cooling the sample from 300 to 30 °C (data were obtained at 10 °C intervals). The storage modulus at a frequency of 10 rad/s was plotted versus temperature, and the sharp decrease in storage modulus indicated the T_{ODT}, which is located as the intersection of two extrapolated lines. Multiple measurements were performed on the same sample to determine the error of the measurement, which was within ±1 °C.

DEFINITIONS

The thermodynamics of polymer blends and block copolymers are described by the following parameters: the composition of the block copolymer or blend, the Flory−Huggins interaction parameter (χ), and the number of repeat units of each component i in the blend or block copolymer (N_i).[59] In this study, χ and N_i are calculated based on a reference volume (v_{ref}) of 100 Å^3, following ref 60. The choice of a constant reference volume (and one that is independent of monomer type) allows for the most direct comparison of χ parameters determined from blends containing polymers of varying molecular structure (and monomer volume). Furthermore, N_i is taken to be the weight-average degree of polymerization ($N_{w,i}$) in the determination of χ from cloud point measurements and number-average degree of polymerization ($N_{n,i}$) in the determination of χ from the order−disorder transition of triblock copolymers (refer to the Results for more details regarding the choice of molecular weight-average in these calculations). To define χ and N_i based on v_{ref}, we will use the following expressions:

$$N_{w,i} = \frac{v_{mon,i}N_{mon,i}}{v_{ref}} = \frac{M_{mon,i}}{\rho_i N_A}\frac{M_{w,i}}{M_{mon,i}}\frac{1}{v_{ref}} = \frac{M_{w,i}}{\rho_i N_A v_{ref}} \quad (1)$$

$$N_{n,i} = \frac{v_{mon,i}N_{mon,i}}{v_{ref}} = \frac{M_{mon,i}}{\rho_i N_A}\frac{M_{n,i}}{M_{mon,i}}\frac{1}{v_{ref}} = \frac{M_{n,i}}{\rho_i N_A v_{ref}} \quad (2)$$

In eqs 1 and 2, $M_{mon,i}$ is the molecular weight of a monomer repeat unit, $v_{mon,i}$ is the volume of a monomer repeat unit, $N_{mon,i}$ is the number of monomer repeat units on the polymer chain, $M_{w,i}$ is the polymer weight-average molecular weight, $M_{n,i}$ is the polymer number-average molecular weight, ρ_i is the polymer density, and N_A is Avogadro's number.

RESULTS

Temperature-Dependence of the Volume of a Monomer Repeat Unit ($v_{mon,i}$). To employ eqs 1 and 2, the densities of the polyacrylates and PS are required. The PS density at room temperature was reported as 1.04 g/mL in ref 61. In a previous publication, we reported a procedure for measuring the densities of PLAc and poly(LAc-*co*-SAc) random copolymers, which were in the range of 0.92−0.94 g/mL at room temperature (around 21 °C).[18] Following the same procedure, the density of PSAc was measured to be 0.92 g/mL. With this information, the room temperature volume of a monomer repeat unit, $v^{o}_{mon,i}$, can be calculated as $v^{o}_{mon,i} = (M_{mon,i}/\rho_i N_A)$. At elevated temperatures, $v_{mon,i}$ will be affected by the thermal expansion of the polymer, which can be calculated using the equation

$$v_{mon,i}(T) = v^{o}_{mon,i}[1 + \alpha_i(T - T^{o})] \quad (3)$$

where $v^{o}_{mon,i}$ is the monomer volume at room temperature, α_i is the volumetric thermal expansion coefficient, T^{o} is room temperature, and T is the temperature of interest. The volumetric thermal expansion coefficient of PS has been reported to be 2.16×10^{-4} and 5.13×10^{-4} K^{-1} for the glassy and rubbery states, respectively.[62] For PLAc, PSAc, and poly(LAc-*co*-SAc), there are no reported values to follow, however, Rogers et al. have studied the thermal expansion coefficients of a series of poly(*n*-alkyl methacrylates).[63] For PLAc and poly(LAc-*co*-SAc), the polymer is in a rubbery amorphous state at room temperature (the melting temperature, T_m, and the glass transition temperature, T_g, are below room temperature); the value of the thermal expansion coefficient is taken as that of poly(lauryl methacrylate) in the rubbery state (6.8×10^{-4} K^{-1}).[63]

For the PSAc homopolymer, which has a T_m of around 50 °C,[18] the thermal expansion coefficients in the semicrystalline and amorphous states were taken to be those of poly(stearyl methacrylate) (PSMA) in the semicrystalline (4.0×10^{-4} K^{-1}) and amorphous (6.2×10^{-4} K^{-1}) states, respectively.[63] Additionally, there is a drastic increase in the specific volume during the melting transition. PSMA exhibited a 4.8% increase in specific volume upon melting:[63] this same increase in specific volume upon melting was applied to PSAc in our study.

For all polymers employed in this study, the temperature-dependent values of $v_{mon,i}$ were used to calculate the temperature-dependent volume fraction (ϕ_i) and N_i of each component in the blend or block copolymer. As the polymers utilized in this study have similar temperature-dependencies of $v_{mon,i}$, the values of ϕ_i did not vary significantly with temperature.

Determination of the χ Parameter from Cloud Point Measurements in Binary Blends. Cloud point experiments were conducted on binary blends of PS and polyacrylate homopolymers. The homopolymer characteristics are summarized in Table 1. Blends were prepared as described in the Experimental Methods with various compositions. The temperature at which the blend transitioned from transparent to opaque (i.e., the cloud point temperature, T_{cp}) was determined using an optical microscope and the results are shown in Figure 1. The blend characteristics are summarized in Tables S2 and S3 of the Supporting Information.

Table 1. Characteristics of Homopolymers Used in Cloud Point Measurements[a]

sample	M_n (kg/mol)	M_w (kg/mol)	$Đ$	N_w (at room temp.)
PS	3.1	3.4	1.11	55.7
PLAc	3.8	4.4	1.15	77.0
PSAc	2.5	2.6	1.05	46.6

[a] M_n, M_w, and $Đ$ were determined from GPC; N_w is the weight-average degree of polymerization (based on a reference volume of 100 Å^3 and using the room temperature densities of the polymers).

The Flory−Huggins theory for the free energy of mixing of two homopolymers A and B is given by refs 30 and 31

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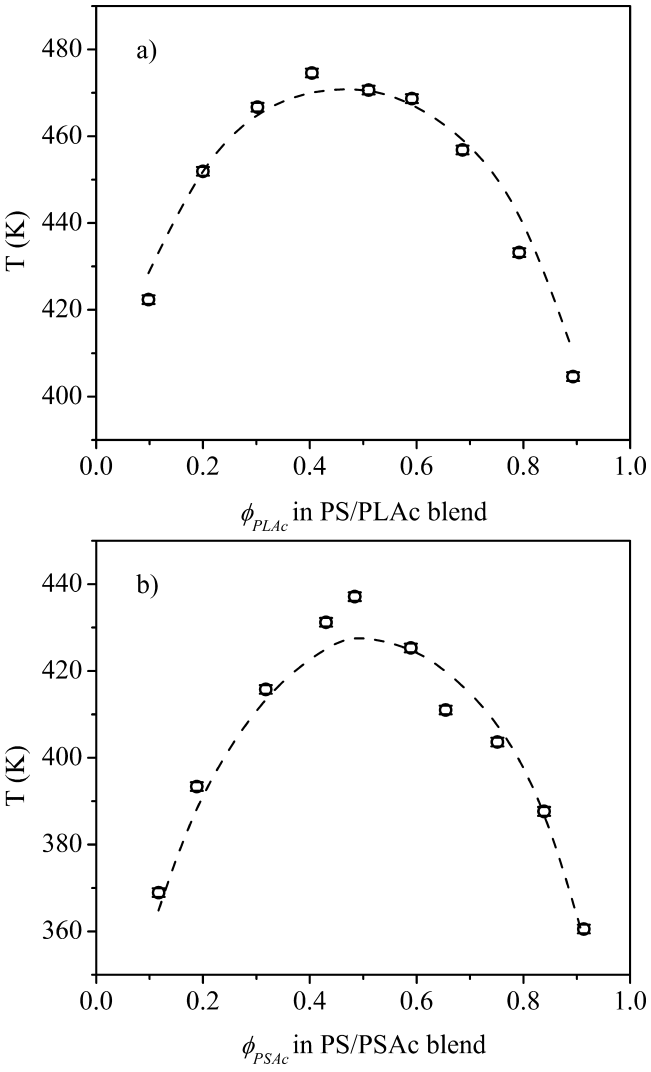

Figure 1. Cloud point temperatures (symbols) of (a) PS/PLAc blends and (b) PS/PSAc blends. The error bars for the cloud point temperature are included, and are approximately the size of the data points. The dashed curves represent the Flory–Huggins theory prediction of the location of the binodal curve, relying upon the results shown in Figure 2 and Figure S6 of the Supporting Information; procedures are described in the text.

$$\frac{\Delta G_m}{kT} = \frac{\phi_A \ln \phi_A}{v_{mon,A} N_{mon,A}} + \frac{\phi_B \ln \phi_B}{v_{mon,B} N_{mon,B}} + \chi \frac{\phi_A \phi_B}{v_{ref}} \quad (4)$$

where ΔG_m is the free energy change on mixing per unit volume, k is the Boltzmann constant, T is the absolute temperature, ϕ_i is the volume fraction of each blend component (i = A or B), $v_{mon,i}$ is the volume of each monomer on chain i, v_{ref} is the reference volume (100 Å^3), $N_{mon,i}$ is the number of monomer repeat units in chain i, and χ is the Flory–Huggins interaction parameter (based on the reference volume v_{ref}).

Using eq 1, eq 4 can be rewritten as

$$\frac{\Delta G_m v_{ref}}{kT} = \frac{\phi_A \ln \phi_A}{N_{w,A}} + \frac{\phi_B \ln \phi_B}{N_{w,B}} + \chi \phi_A \phi_B \quad (5)$$

The binodal curve was constructed by deriving expressions for the chemical potentials of each component in the blend using eq 5 and equating the chemical potentials for each component in phases I and II:[60]

$$\ln \frac{\phi_A^I}{\phi_A^{II}} + (\phi_A^{II} - \phi_A^I)\left(1 - \frac{N_{w,A}}{N_{w,B}}\right) + \chi N_{w,A}[(1 - \phi_A^I)^2 - (1 - \phi_A^{II})^2] = 0 \quad (6)$$

$$\ln \frac{1 - \phi_A^I}{1 - \phi_A^{II}} + (\phi_A^I - \phi_A^{II})\left(1 - \frac{N_{w,B}}{N_{w,A}}\right) + \chi N_{w,B}[(\phi_A^I)^2 - (\phi_A^{II})^2] = 0 \quad (7)$$

Simultaneously solving eqs 6 and 7 resulted in the determination of ϕ_A^I and ϕ_A^{II} as a function of χ. The results of this calculation are shown in Figure S6 of the Supporting Information. We have chosen to use the weight-average degree of polymerization, N_w, in these calculations as larger sized molecules will drive the phase separation of polymer blends. A comparison of the cloud point data (Figure 1) and the theoretical binodal curve (Figure S6 of the Supporting Information) gives the relationship between χ and T, reported in Figure 2.

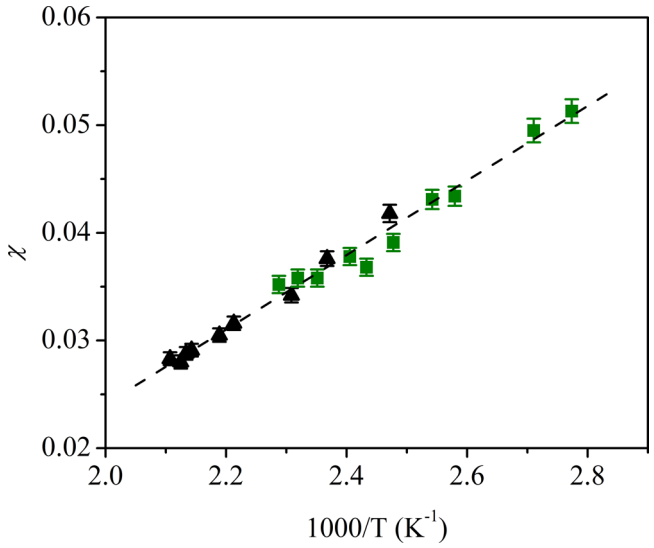

Figure 2. χ as a function of inverse temperature for PS/polyacrylate blends from cloud point measurements: PS/PLAc binary blends (black ▲); PS/PSAc binary blends (green ■). χ is based on a reference volume of 100 Å^3. The error bars are included and in many cases are smaller than the data points. The data have been fit to a linear equation (dashed line): $\chi = (34.6/T) - 0.0451$.

There are three categories of errors to consider in this measurement of χ: (1) error in the molecular weight measurement from GPC, (2) error in the cloud point measurement, and (3) error in the thermal expansion coefficient. For the GPC measurement, the error has been found to be within ±2% by multiple measurements. The error in cloud point measurement was within ±1 °C for all experiments. In this study, we do not quantify the error in the thermal expansion coefficient, which was taken from a literature source. The cumulative error is summarized in Tables S2 and S3 in the Supporting Information and shown as error bars in Figure 2. The $\chi(T)$ curves for both polyacrylates are consistent with one another, indicating the behavior of $\chi(T)$ is independent of the side chain length of polyacrylates.

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Table 2. Characteristics of SAS Triblock Polymers Used in Rheology Measurements

polymer	M_n (kg/mol)[a]	$Đ$[a]	ϕ_{PS} at room temp[b]	midblock M_n (kg/mol)[a]	midblock $Đ$[a]	LAc wt % in midblock[b]
SAS(1−1)	76.2	1.67	0.230	57.3	1.26	100
SAS(1−2)	70.4	1.44	0.171	57.3	1.26	100
SAS(1−3)	48.7	1.38	0.180	39.2	NA[c]	100
SAS(2−1)	78.4	1.65	0.239	58.2	1.30	76
SAS(2−2)	72.3	1.43	0.180	58.2	1.30	76
SAS(2−3)	49.0	1.42	0.179	39.5	NA[c]	73
SAS(3−1)	75.7	1.61	0.231	56.8	1.28	61
SAS(3−2)	70.7	1.42	0.181	56.8	1.28	61
SAS(3−3)	48.3	1.44	0.181	38.8	NA[c]	62
SAS(4−1)	81.1	1.38	0.241	59.7	1.26	0
SAS(4−2)	73.2	1.44	0.167	59.7	1.26	0
SAS(4−3)	47.7	1.42	0.206	36.9	1.20	0
SAS(4−4)	70.7	1.38	0.141	59.7	1.26	0
SAS(4−5)	69.0	1.44	0.121	59.7	1.26	0

[a]Determined with GPC (light scattering). [b]Determined with ^{1}H NMR. [c]The triblock copolymer was synthesized through chain extension from PS (see ref 18) and the midblock $Đ$ cannot be measured.

Determination of the χ Parameter from the Order−Disorder Transition (ODT) of Triblock Copolymers. Four series of triblock copolymers were investigated, with the polymer characteristics given in Table 2. The order−disorder transition temperatures (T_{ODT}) of the polymers (determined through rheology as described in the Experimental Methods) are summarized in Table S4 of the Supporting Information. Figure 3 shows a representative data set, with the storage modulus plotted as a function of temperature for SAS(4−1). The rheology data for the other samples are either provided in the Supporting Information (Figure S7) or, in some cases, were previously reported in ref 18.

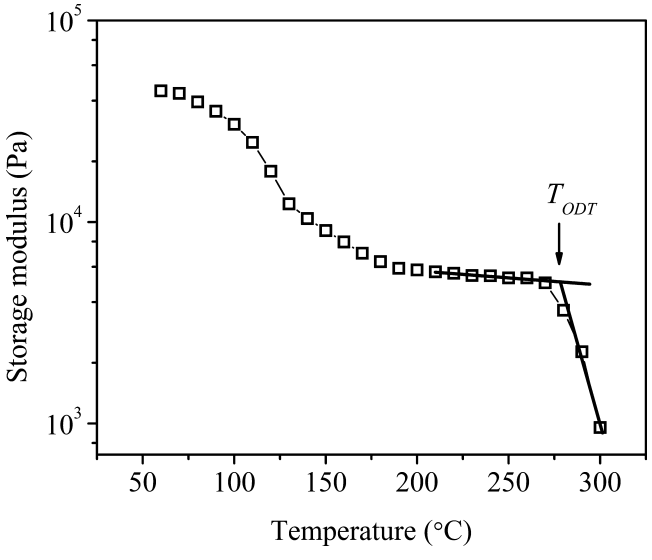

Figure 3. Storage modulus as a function of temperature of triblock copolymer SAS(4−1). The T_{ODT} was determined as the intersection of the two extrapolated lines.[64]

The theoretical ODT of a triblock copolymer is defined by the composition (volume fraction of each block), and the thermodynamic parameter χN, where N is the number of total repeat units on the triblock copolymer (taken to be N_n in this study, following many prior studies on block copolymer thermodynamics).[65] With knowledge of the triblock copolymer N_n and composition, the predicted χ value at the order−disorder transition for each SAS triblock copolymer was calculated (Table S4 in the Supporting Information). Using the χ value at the ODT and experimental T_{ODT} values, the relationship between T_{ODT} and χ was constructed (additional information is provided in the Supporting Information).

There are still many open questions regarding the effects of dispersity on the block copolymer phase diagram.[66] We have chosen to compare χ parameters calculated using two different theoretical triblock copolymer phase diagrams determined from self-consistent field theory: (1) the standard phase diagram of a monodipserse triblock copolymer, described in ref 65, and (2) the phase diagram for a triblock copolymer containing monodisperse end-blocks and a disperse midblock ($Đ$ = 1.5), described in ref 67. Neither theoretical phase diagram is directly applicable to our SAS triblock copolymers, in which the polyacrylate midblock $Đ \approx 1.2-1.3$ (Table 2), the outerblock PS $Đ \approx 1.1$ (based upon characterization of PS homopolymers synthesized using the same methods), and the triblock copolymer molecular weight distribution is trimodal (described in more detail in ref 18).

Figure 4 and Table S4 in the Supporting Information show χ versus $1/T$ for SAS triblock copolymers of different midblock compositions (varying the wt % LAc in the midblock), using the theoretical phase diagram of a monodisperse triblock copolymer, taken from ref 65. The calculated χ versus $1/T$ using the phase diagram for a triblock copolymer containing a disperse midblock ($Đ$ = 1.5), described in ref 67, is included in Figure S8 and Table S5 of the Supporting Information. Regardless of the theoretical phase diagram used in calculation of the χ parameters, it is clear that the $\chi(T)$ curves for all of the triblock copolymers are consistent with one another. The behavior of $\chi(T)$ is thus independent of the midblock composition of the triblock copolymer.

The error in the χ measurement was also evaluated and can be divided into four categories: (1) error in T_{ODT} from the rheology measurement, (2) error in molecular weight and volume fraction measurement from GPC and NMR, (3) error in the thermal expansion coefficient of each component, and (4) error in determining the theoretical χN. Multiple measurements of T_{ODT} have been taken on the same sample, and the error in T_{ODT} was within ±1 °C. Multiple measurements of molecular weight and volume fraction were also performed and the errors for both were within ±2%. We

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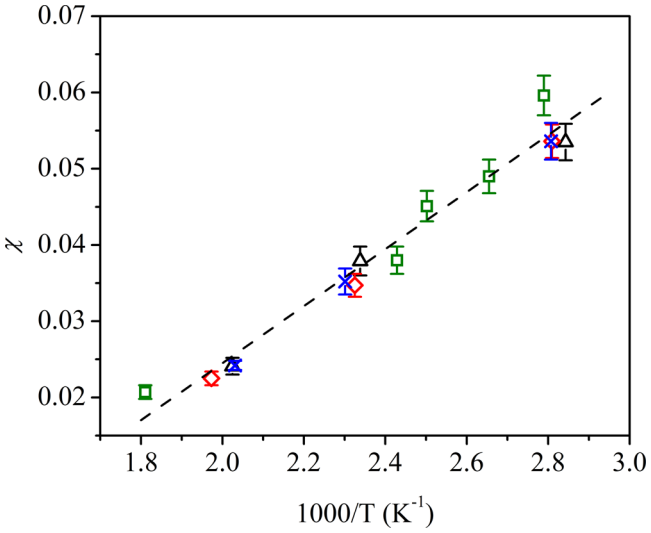

Figure 4. χ as a function of inverse temperature determined from ODT measurements on SAS triblock copolymers (based on theoretical phase diagram in ref 65): 100% LAc in the midblock (black △); 76% LAc in the midblock (red ◊); 61% LAc in the midblock (blue ×); 100% SAc in the midblock (green □). χ is based on a reference volume of 100 Å^3. The error bars are included and in some cases are smaller than the data point. The data have been fit to a linear equation (dashed line): $\chi = (37.4/T) - 0.0503$.

are not able to evaluate the third category in this study, as we are drawing from the literature for the values of the thermal expansion coefficient. The uncertainty in determining χN from the theoretical phase diagram is potentially significant, and we have not attempted to quantify this error. Rather, in Figure S8 (Supporting Information), we have compared the results using two different theoretical phase diagrams of triblock copolymers with differing molecular weight distributions. The results from the first two categories of errors are summarized in Tables S4 and S5 of the Supporting Information and shown as error bars in Figure 4 and Figure S8 (Supporting Information).

DISCUSSION

Figures 2 and 4 represent the temperature-dependent χ parameters measured for PS and long-chain poly(*n*-alkyl acrylates). The poly(*n*-alkyl acrylates) included in this study are PLAc, PSAc, and poly(LAc-*co*-SAc) random copolymers. Importantly, the poly(*n*-alkyl acrylates) differ in the length of the side-chain on each repeat unit (12 and 18 carbon atoms for PLAc and PSAc, respectively). χ parameters determined from cloud point measurements on binary blends and ODT measurements on triblock copolymers lie on one line in Figures 2 and 4 (within the error of the χ measurement). This indicates that the length of the side-chain (n) of the polyacrylate has little effect on the thermodynamic interactions between PS and the poly(*n*-alkyl acrylates) at large values of n.

To explore the side-chain length-dependence of the χ parameter, we have employed group contribution methods to calculate the solubility parameters (δ) of poly(*n*-alkyl acrylates) as a function of the side-chain length, n, shown in Figure 5. We have followed similar procedures to that described in ref 32 (using the van Krevelen parameters in ref 68). The results of our calculations are in good agreement with refs 57 and 32, which included side-chain lengths up to n = 10. Our calculations indicate that at higher values of n (>10), the solubility parameter continues to decrease slightly with

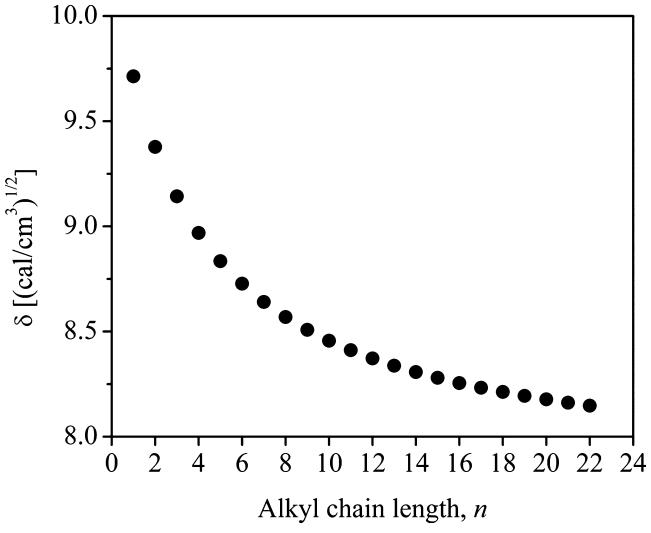

Figure 5. Solubility parameter (δ) of poly(*n*-alkyl acrylates) as a function of alkyl chain length (n).

increasing n. Additionally, we have calculated δ of PS using the same methods (δ = 9.3).

The χ parameter was calculated using eq 8

$$\chi = \frac{v_{ref}}{kT}(\delta_1 - \delta_2)^2 \quad (8)$$

where δ_1 and δ_2 are the solubility parameters of components 1 and 2, the reference volume was chosen to be 100 Å^3, and k is the Boltzmann constant.

Figure 6 compares the χ parameter at 120 °C for PS and poly(*n*-alkyl acrylates) as a function of the alkyl side-chain

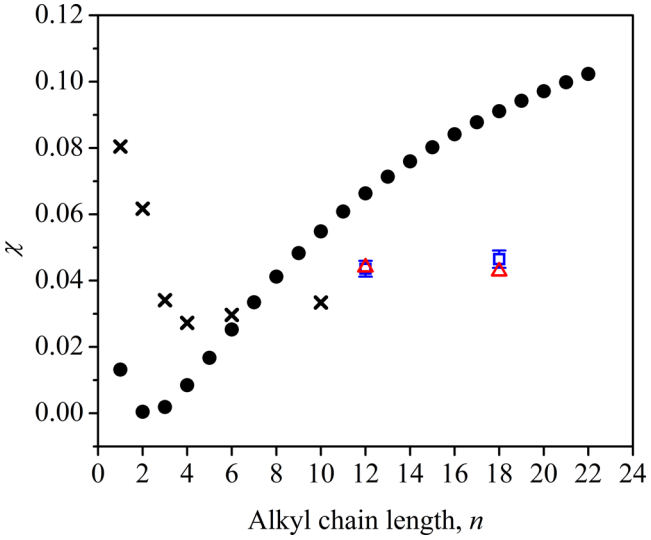

Figure 6. Effect of alkyl chain length on χ of PS and poly(*n*-alkyl acrylates) (v_{ref} = 100 Å^3). χ was calculated using solubility parameters (black ●); calculated from binary interaction energy densities (determined by the copolymer/critical molecular weight method) reported in ref 32 (black ×); and measured in this study through characterization of the ODT of triblock copolymers (blue □) and cloud point measurements on binary blends (red Δ).The error bars have been included for this study (n > 10): for the ODT measurements (blue □) the error bars are slightly larger than the data points and for the cloud point measurements (red Δ) they are smaller than the data points.

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length, n. We have included χ parameters in Figure 6 from three different sources: (1) calculated from the solubility parameters given in Figure 5 (using eq 8), (2) experimentally measured for short-chain poly(n-alkyl acrylates), reported in ref 32 (we have calculated the χ parameter using the binary interaction energy density reported in ref 32 and a reference volume of 100 Å^3), and (3) experimentally measured for long-chain poly(n-alkyl acrylates) in our study (i.e., Figures 2 and 4). Additionally, in Figure S9 of the Supporting Information, the related binary interaction energy density is plotted as a function of n for the same polymer pairs.

It is clear that there are strong deviations between the χ parameters calculated using solubility parameter theory and the experimentally measured values, consistent with the conclusions of ref 32 for poly(n-alkyl acrylates) with $n \leq 10$. Other studies have compared the solubility parameters for a variety of polymers determined experimentally (i.e., through PVT measurements, scattering, cloud point experiments, inverse gas chromatography, among other methods) with those predicted from group contribution methods. In some cases there is good agreement,[68−71] and in other cases there are significant deviations between theory and experiment.[68,72−74] We also note that prediction of the χ parameter from solubility parameter theory (regardless of the source of the solubility parameter) does not always agree with direct measurement of the χ parameter, most notably in systems with a negative χ parameter.[75,76] The results of our study indicate that group contribution methods, combined with solubility parameter theory, do not capture the thermodynamic behavior in blends of polystyrene and long-chain poly(n-alkyl acrylates).

The experimentally measured χ parameters reported in this manuscript are effective χ parameters, which do not strictly follow the Flory−Huggins definition of χ, but are fitting parameters that also account for additional contributions to the free energy of mixing not described by Flory−Huggins Theory. Oftentimes the empirical equation used in our study to describe the temperature-dependence of χ ($\chi = A/T + B$) is thought of in terms of an enthalpic contribution (i.e., A/T) and an entropic contribution (i.e., B). It may be more appropriate to directly compare the experimental enthalpic A/T term to the predictions from solubility parameter theory (i.e., eq 8). If we consider only the enthalpic A/T portion of our experimentally measured $\chi(T)$ equations, we obtain similar values at 120 °C for polyacrylates with n = 12 and 18 (A/T = 0.095 and 0.090 for PLAc and PSAc, respectively; refer to Figure S10 in the Supporting Information in which the data sets are analyzed separately). Though these values are closer in magnitude to the χ parameters predicted by the group contribution methods for n = 12 and 18 (0.066 and 0.091 for PLAc and PSAc, respectively), there is still an important disconnect between the theory and experiment: the group contribution method predicts that χ increases with increasing n (at high n), whereas the experimental measurement (even when only considering the enthalpic A/T term) shows that χ is independent of n (at high n). Furthermore, the observation of a non-negligible B term is oftentimes associated with the presence of additional contributions to the entropy of mixing, such as differences in molecular packing of the pure component and mixed states. These effects may be important in these systems, but the magnitude of the B term in the $\chi(T)$ equation is similar for polyacrylates with n = 12 and 18 (B = −0.051 and −0.047 for PLAc and PSAc, respectively; refer to Figure S10 in the Supporting Information in which the data sets are analyzed separately). Differences observed in the A and B parameters extracted for the fit of the $\chi(T)$ equation to data obtained from each individual blend (or similarly, block copolymer), shown in Figure S10 of the Supporting Information, reflect the error of measuring χ that has been quantified in this study.

The χ parameter for PS and PLAc (or PSAc) was characterized using two independent methods: ODT measurements on triblock copolymers and cloud point measurements on binary blends. The χ parameters determined from binary blends and block copolymers are quite similar to one another, though the level of quantitative agreement between them depends on the choice of theoretical phase diagram for the triblock copolymers (i.e., compare Figures S8a and S8b in the Supporting Information). The ability to generate a linear curve describing the temperature-dependence of χ (i.e., $\chi = A/T + B$), as shown in Figures 2 and 4, through measurements on blends and block copolymers of varying composition, which contain polymers of varying molecular weight, indicates that these χ parameters are relatively insensitive to molecular weight and composition effects.

Importantly, we can conclude that at longer side-chain lengths ($n > 10$), the χ parameter is independent of the alkyl side-chain length, n. To our knowledge, this is the first study to explore the thermodynamic interactions between PS and long-chain poly(n-alkyl acrylates) with $n > 10$. The characterization of the Flory−Huggins interaction parameter is an essential first step to the design of microstructured or nanostructured materials in multicomponent systems, guided by predictions of theories, such as self-consistent field theory.[77−79] Importantly, our work highlights the necessity for alternative theories to understand the origins of the behavior in this class of materials.

CONCLUSIONS

Two independent methods were employed to calculate the Flory−Huggins interaction parameter (χ) between polystyrene (PS) and long-chain poly(n-alkyl acrylates): cloud point measurements on binary blends and characterization of the order−disorder transition of triblock copolymers. The poly(n-alkyl acrylates) included in this study were poly(lauryl acrylate) (PLAc), poly(stearyl acrylate) (PSAc), and poly(LAc-*co*-SAc) random copolymers. Importantly, the poly(n-alkyl acrylates) differ in the length of the alkyl side-chain on each repeat unit (12 and 18 carbon atoms for PLAc and PSAc, respectively). The χ parameter was found to be independent of the alkyl side-chain length (n) for large values of n. This behavior is in stark contrast to the n-dependence of the χ parameter predicted from solubility parameter theory. To our knowledge, this is the first study to explore the thermodynamic interactions between PS and long-chain poly(n-alkyl acrylates) with $n > 10$. In addition, the χ parameter appears to be relatively insensitive to polymer chain architecture, molecular weight, and composition in this system, as the temperature-dependence of the χ parameter was extracted from blends and block copolymers in which all of these parameters were varying. This work lays the foundation for future studies to examine blends or block copolymers consisting of long-chain poly(n-alkyl acrylates) and various other constituents, including the examination of systems containing multiple components with long side-chains. The implementation of polymers derived from fatty acids and vegetable oils in multicomponent materials, such as blends and copolymers, will rely upon a detailed understanding of the thermodynamic interactions in such systems.

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■ ASSOCIATED CONTENT

Supporting Information

Representative GPC traces for a SAS triblock copolymer (Figure S1), PLAc used in cloud point measurements (Figure S2), PSAc used in cloud point measurements (Figure S3), and PS used in cloud point measurements (Figure S4); NMR data and characterization of meso and racemo dyads in PLAc and PSAc (Figure S5 and Table S1); cloud point blend characteristics and results (Tables S2 and S3); Flory−Huggins theory prediction of the binodal curve χ vs composition in binary blends (Figure S6); storage modulus as a function of temperature used in the ODT determination of SAS triblock copolymers (Figure S7); summary of χ parameters determined from rheology measurements (Tables S4 and S5); comparison of $\chi(T)$ from different methods (Figure S8); binary interaction energy density as a function of alkyl side-chain length (Figure S9); and linear fit of $\chi(T)$ using data sets for each individual sample and characterization method (Figure S10). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b02326.

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Notes

The authors declare no competing financial interest.

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