Polymer 124 (2017) 235–245

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

The glass transition temperatures of amorphous linear aliphatic polyesters

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ARTICLE INFO

Article history:
Received 26 April 2017
Received in revised form
10 July 2017
Accepted 21 July 2017
Available online 22 July 2017

Keywords:
Glass transition
Amorphous linear aliphatic polyester
Conformational entropy

ABSTRACT

A series of wholly amorphous linear aliphatic co- and tetra-polyesters were synthesized *via* bulk melt step-growth polymerization. Their glass transition temperatures were determined using DSC and were essentially unaffected by crystallinity. The glass transition temperatures of the polyesters increase linearly with the ratio of ester groups per methylene group. Extrapolations of the ratio to zero ester group content gave a reliable value for the T_g of amorphous polyethylene (PE). The experimental T_gs manifest a steeper slope on the T_g *vs.* ester group content plot compared to those calculated using Van Krevelen's group contribution method. The intramolecular equilibrium flexibilities were evaluated through the calculation of conformational entropies of individual polymer chains approximated by considering solely the short-range interactions between neighboring groups, as embodied in their RIS conformational models. Their calculated conformational entropies, S_{conf}, decrease linearly with increasing ester group content, leading to the observation that $S_{conf} \propto 1/T_g$.

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1. Introduction

Despite the long history of recognizing the profound effects of chemical structure on the glass transition of polymers, modern theories have yet to develop direct connections between model compounds and a myriad of real polymers of practical importance, exceptions being only the simplest monomeric structures. The reason for this lag of theoretical understanding is two-fold:

Firstly, factors pertinent to the molecular bases of polymer glass formation are usually structurally interdependent; it can be difficult to isolate a single effect when comparing different chemical structures. ***e.g.,*** the following factors are commonly suggested as being pivotal: **1.** The inherent conformational flexibilities of individual polymer chain backbones; **2.** The sizes, steric bulk, and the relative flexibility of their side-chains; and **3.** The interactions (steric, dipolar, hydrogen-bonding, van der Waals, etc.) between polymer chains [1,2]. We have to be aware that more than one of the above factors, and likely all three, will be distinct by changing the monomeric structure. This difficulty has been clearly recognized in very recent experimental and theoretical examinations of the molecular bases for polymer glass formation [3–6].

Secondly, experimental studies performed on polymers whose microstructures were controlled in a manner that permit systematic assessments of the individual structural contribution to polymer glass formation are scarce, so the relative importance of each factor on the glass formation of real polymers is largely unknown. Undoubtedly, the lack of this experimental information deprives theoreticians of the ability to test a theory's predictive power against the glass-transition behaviors of real polymers.

In order to select model polymers that differ in only a single structural feature, sufficient theoretical or experimental evidence indicating the similarities of all other factors except the one being compared need to be established. Consider atactic poly(styrene/p-Br-styrene) copolymers obtained by bromination of atactic polystyrene (PS) as an example. Because of the large distances between p-Br in the side-chain and the atoms in the backbone, the conformations of all copolymers are closely similar, independent of composition and sequence of the S and *p*-BrS units [7]. This can be confirmed by their invariant backbone carbon ^{13}C NMR chemical shifts and by their very similar zero-shear viscosities [8]. Hence their T_gs should not be affected by 1. inherent chain flexibilities, but only by 2. side-chain size and 3. inter-chain interactions. The combination of these two factors cause their T_gs to range linearly with composition from 97.2 °C for PS to 140.1 °C for Poly(*p*-BrS) [9],

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http://dx.doi.org/10.1016/j.polymer.2017.07.054
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and are independent of comonomer sequences [8,9].

In another study, the T_gs of polystyrene partially sulfonated in the para position have been found to increase linearly with the percent of sulfonation [10]. The linearity of copolymers' T_g dependence on composition irrespective of their comonomer distribution and the chemical nature of the substituents confirmed that conformational characteristics were unaffected and that the sizes and interactions contributed in the same manner, though with presumably a different magnitude, to the increase of the T_gs of the copolymers. A recent experimental study [5] confirmed this point. Comparisons among Polystyrene (PS), poly(4-methystyrene) (P4MS), and poly(4-chlorostyrene) (P4ClS) are uncomplicated by distinct conformational flexibilities, while T_g comparisons between other polymers have non-trivial dependences. *e.g.*, the substitutions in ortho- and meta-position augment the effect of substituent sizes on the intrinsic backbone flexibilities, which outweigh the effect of polar interactions on the increased T_gs.

To sum up, one has to have adequate information regarding the effects of different structural factors on the polymer backbone flexibility before any conclusion can be drawn about the relative importance of the particular structural factor on glass formation.

At this point, it is necessary to examine with “due diligence” how the backbone flexibility was evaluated in prior studies. When Flory [11] pointed out the important role chain inflexibility or stiffness plays in the crystallization of polymers, a flexibility factor, f, was defined as the fraction of bonds bent out of their low energy co-linear position. f is simply the probability of the bond adopting an energetically un-favored conformation with an energy penalty ε weighted through a Boltzmann factor. Gibbs [12] and DiMarzio [13] (GD) later replaced solvents with holes in adapting Flory's lattice formulation and interpreted T_g as an ideal thermodynamic transition of the vanishing number of arrangements when the flexibility factor reaches a lower limit, below which the system become unphysical. GD theory met with success in replicating qualitatively many aspects of the glass transition. Clearly, this decrease in f while temperature is lowered promotes the rapid decrease in the number of arrangement available for packing a rigid chain.

Similarly, Freed and co-workers [14–17] incorporate semi-flexibility into the lattice cluster theory (LCT) using a bending energy, E_b, as the energy difference between trans and gauche conformations. However, difficulties [16,17] arose in prescribing bending energy to structured monomers; *e.g.*, presence of side chains. In their most recent study [4], two separate bending energies, E_b and E_s, were assigned to backbones and side chains, though these two parameters may not be independent as assumed in their treatment.

Another lattice-based model, *i.e.*, White and Lipson's [18,19] locally correlated lattice (LCL) model, does not include explicit terms for polymer flexibilities. A close examination reveals that their three molecular parameters, which are used as adjustable parameters for fitting experimental PVT data, must include the effect of chain flexibility through the variation in r, the number of effective segments per chain molecule, and v, the volume per lattice site or similarly the temperature-independent hard-core volume of the segment.

Schweizer and coworkers' elastically collective nonlinear Langevin equation (ECNLE) theory [6,20] utilized the Kuhn length, l_k, and the number of interaction sites in a Kuhn segment, N_s to account for the molecular information of model polymers. In addition to Kuhn length, the characteristic ratio, C_∞, has been widely used as a parameter for characterizing chain flexibility in the literature [21–23] of polymer glass transitions. In the phenomenological application of mode coupling theory (MCT) using molecular dynamics (MD) simulation [23], λ-exponents, whose value is indicative of the underlying mechanisms, obtained for polymers increase monotonically with increasing intramolecular barriers starting from fully flexible bead-spring chains, whose value is close to the values typical for small molecules. Connectivity alone does not give rise to the higher value of λ-exponents for semi-flexible polymers; leaving intramolecular rotational barriers accountable [24]. Characteristic ratios, as an evaluation of chain flexibility, were calculated directly from mean squared end-to-end distances obtainable through simulations and are shown to have positive correlation with the calculated λ-exponents. Despite its many successful applications as an indicator of chain flexibility, characteristic ratio itself is instead a measure of chain dimension, which depends not only on chain flexibility but also on chain geometry. In real polymer systems, an inflexible chain could be stuck with high barriers in its lowest energy states that is not the trans conformation of the backbone bonds and thus generates compact chain dimension, *i.e.*, small C_∞.

From the above survey, we conclude that methods developed in the literature to account for the flexibility of polymer chains in the study of their glass transitions were either far from representing real chemical structures or were embedded implicitly in unified parameters, *i.e.*, coarse grained. A successful statistical mechanical computational method, the Rotational Isomeric State (RIS) Model, developed by Flory [25] offers a realistic account of the effect of chemical structure on the intra-chain conformational characteristics of polymers. All RIS conformational models start from knowledge of bond angles, bond lengths, torsional angles and applicable interaction potentials of short chain analogs.

We wish to begin by setting an example for selecting polymers that are structurally well controlled, so that their conformational flexibilities are fixed or can be easily evaluated and tracked using RIS models. The inherent conformational flexibilities of RIS models of structurally analogous linear aliphatic polyesters and polyamides are virtually identical [25,26]due to the fact that ester and amide bonds both contain partial double bond character, are rigid and therefore result in similar planar structures with a *trans* conformation [25]. For example, poly(ε-caprolactone) (PCL) and poly(ε-caprolactam) (nylon-6) have similar calculated overall conformational preferences and do not possess side chains. Therefore, aside from possible dissimilar effects of crystallinity, their ~100 °C difference in T_gs can be attributed to the relative effect of hydrogen-bonding *vs*. dipole-dipole inter-chain interactions. Glass transition temperatures of structurally analogous n-nylons and n-polyesters are available and meet the foregoing criteria. When the structure approaches polyethylene (PE), however, crystallinity often complicates the comparisons, as evidenced by the increase in polyesters T_gs with decreasing ester group content.

The profound effect of crystallinity on polymer glass transition temperatures calls for the need to synthesize wholly amorphous samples for the purpose of studying their glass transition. However, in almost all instances amorphous samples were only obtained using divergent chemical structures, including different stereo-sequences or tacticities [27], double bonds [28], and ring structures [29,30], which prevented the separate assessment of the potential structural factors suggested to influence their glass transition temperatures. We attempted to synthesize high molecular weight, amorphous, linear, aliphatic co-polyesters or co-polyamides using monomers that have mismatched numbers of methylene groups to prevent their crystallization. Our trials using monomers with medium to long successions of methylene groups, which are widely used in commercial semi-crystalline applications, fail to produce wholly amorphous samples without the aid of rapid quenching.

Recently, completely amorphous linear aliphatic copolyesters were reported [31]. When ethylene glycol and 1,3-propanediol in the ratios of 40:60 to 20:80 were reacted with succinic acid *via* direct polycondensation reaction with titanium tetraisopropoxide

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