Cooperativity of dynamics in supercooled polymeric materials and its temperature dependence predicted from a surface controlled model

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ABSTRACT

Relation between cooperativity and fragility of segmental dynamics is a crucial issue in elucidating the viscous slowdown of supercooled polymer liquids. The experimental results previously reported for p-substituted polystyrenes (PS derivatives) and poly(methacrylic acid ester)s (PMAEs) are reanalyzed based on a cooperative string model that was recently proposed on the assumption that the cooperatively rearranging region (CRR) takes a string shape. The analysis shows clear positive correlations between the cooperativity and fragility for both the polymer systems. To investigate the temperature dependence of the cooperativity, we proposed a simple model where the size of the CRR is controlled by its surface area (surface-controlled CRR model: SCC). The analysis based on this model suggests that for many of the polymers, the CRR takes a non-compact shape with high surface-to-volume ratio. The configurational entropy of the smallest CRR is also evaluated from calorimetry based on the SCC model, and it is revealed to depend on the segmental relaxation time very weakly compared with that for typical non-polymeric glass-formers.

1. Introduction

Elucidation of the mechanism of glass transition as a fundamental dynamic property of supercooled liquids is one of the most challenging issues in soft matter physics. The α-relaxation in supercooled liquids generally exhibits non-Arrhenius behavior, which leads to a drastic increase in viscosity on cooling and abrupt vitrification at a certain temperature (glass transition temperature T_g) [1]. The non-Arrhenius feature of supercooled liquids is evaluated quantitatively by a fragility parameter m, which is defined as $m = \mathrm{d}\log_{10}\tau/\mathrm{d}(T_g/T)|_{T = Tg}$, where τ is the α-relaxation time [2]. Adam and Gibbs proposed a model that is based on the configurational entropy of supercooled system to understand the drastic viscous slowdown [3]. In this model, a cooperatively rearranging region (CRR) is assumed, within which molecules (segments) can rearrange cooperatively without affecting its surrounding region. The cooperativity in dynamics is often evaluated as the size of the CRR or as the number of segments in the CRR (N_{CRR}). If the cooperativity depends strongly on temperature, the viscous slowdown phenomenon can be qualitatively explained. However, the Adam-Gibbs model does not predict this temperature dependence quantitatively if the temperature profile of configurational entropy is not known.

Furthermore, some shortcomings of the model have been pointed out [4]. Nevertheless, the Adam-Gibbs idea is considered to serve as a basically reasonable understanding of the dynamics of supercooled liquids, and there have been developments in the entropy-based theory [5–7]. On the other hand, there have been experimental efforts to investigate the cooperativity and its temperature dependence by using various advanced techniques [8–16]. We should also note that the cooperativity parameters obtained from different techniques are not consistent with each other in some cases [17].

The cooperative dynamics is a characteristic feature of supercooled liquids, and this uniqueness is considered to originate from the non-ergodicity of supercooled liquids. Below a certain temperature (such as the crossover temperature in the mode coupling theory [18–20]), any two neighboring segments do not have enough energy to be separated completely. As a result, in this temperature regime, an energy landscape with metastable states dominates segmental dynamics giving rise to non-ergodicity [21]. Based on such a scenario, theoretical developments have been achieved [5,7,22,23]. As the above transition temperature has not been directly observed via experiments, it seems to be important to connect it to some phenomenological parameter such as the Vogel temperature.

The materials that exhibit vitrification include metallic, inorganic, organic, and polymeric materials. As an effective clue to elucidate the fundamental mechanism of glass transition, one should find out some universality in dynamical behaviors over a wide range of materials. To this end, the relationship between cooperativity at T_g and fragility has been investigated [24–26]. Unfortunately, any universal trends in a wide variety of polymers have not been found so far, probably because of their complex interaction between the segments. Such complexity in segmental interactions in polymers may be responsible for a tendency to show high fragility [27,28]. On the other hand, studies have been done to interpret and predict the glass transition parameters of polymers on the basis of chemical structures [29–33]. For polymers with similar chemical structures such as poly(n-alkyl methacrylate)s and polystyrene (PS) derivatives were reported to exhibit distinct positive correlations between the two parameters, $N_{CRR}(T_g)$ and m [34–36]. Furthermore, it was found that for para-substituted PS derivatives, bulkiness of the substituent hinders stacking of phenyl groups leading to reduction in the dynamical cooperativity [36].

In this study, we revisit the relation between $N_{CRR}(T_g)$ and m for a series of polymers with identical backbone structures, i.e., poly(methacrylic acid ester)s (PMAEs) and PS derivatives that we reported previously [36], and discuss the origin of positive correlations between the two parameters. In the entropy-based model, the temperature dependence of N_{CRR} plays an important role in determining the relation between the two parameters. Thus, we propose a simple model (surface controlled CRR model) to predict the temperature dependence of N_{CRR}, and to discuss the shape of the CRR. In addition, using the reversing heat capacity data of the above two polymer systems that were obtained by using temperature-modulated differential scanning (TMDSC) technique, temperature dependence of the configurational entropy of the smallest CRR is evaluated on the basis of the SCC model.

2. Experimental

The polymers used in this study were purchased from Scientific Polymer Products, Co. PS derivatives have various para-substituents and PMAEs have various end ester parts in the side group. The average molecular weights (M_n and M_w) determined by size exclusion chromatography, and the volume per repeating unit (segment) V_m are listed in Table 1. All the samples were purified via reprecipitation and freeze-drying methods prior to calorimetry measurements. The detailed procedures are described in Ref. [36]. Cooperativity as a length scale ξ at T_g and fragility m were evaluated via DSC measurements as described in

Table 1
Average molecular weights and segmental volume of polymers.

Polymer[a]	M_n/kDa	M_w/kDa	V_m/nm³
a-PS	425[b]	451[b]	0.165
i-PS		400[b]	0.165
s-PS		300[b]	0.165
PMS	30.4	103	0.188
PMOS	59.0	127	0.221
PtBS	43.6	274	0.280
PClS	39.6	79.3	0.149
PBrS	33.1	61.1	0.216
a-PMMA	292[b]	298[b]	0.138
i-PMMA	44.3	159	0.136
s-PMMA	42.9	56.6	0.140
PEMA	90.4	222	0.172
PiPMA	50.2	110	0.206
PnBMA	69.8	165	0.220
PsBMA	33.2	90.4	0.224
PPhMA	25.9	71.9	0.222
PBzMA	35.9	124	0.248
PCHMA	26.5	95.0	0.254

[a] The polymers are atactic unless specified.

[b] Data from manufacturer's data sheet.

Table 2
Exponent d estimated on the basis of the string model.

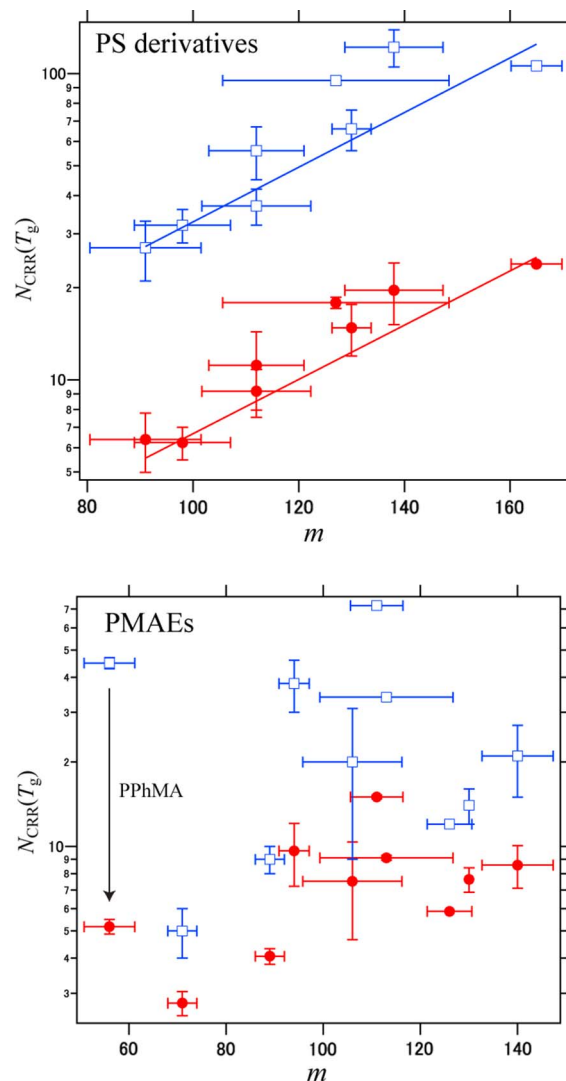| Polymer	d
a-PS	1.9
i-PS	2.0
s-PS	1.9
PMS	1.9
PMOS	1.9
PtBS	1.8
PClS	1.8
PBrS	1.7
a-PMMA	1.9
i-PMMA	1.9
s-PMMA	2.2
PEMA	2.1
PiPMA	1.9
PnBMA	2.0
PsBMA	2.4
PPhMA	1.3
PBzMA	1.9
PCHMA	2.2

Fig. 1. $N_{CRR}(T_g)$ plotted against m for PS derivatives and PMAEs. The open squares (blue) indicate the values obtained with $d = 3$, and filled circles (red) indicate those obtained from the d values in Table 2. The solid lines are the results of linear regression. The arrow in the lower panel shows a noticeable shift for PPhMA. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)