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Constraint dynamics and chemical structure

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Abstract

The effect of chemical structure on the segmental relaxation behavior is examined for a wide range of polymers. Both the time and temperature dependence of the glass transition dispersion in the dielectric loss spectrum are shown to be correlated with the degree to which local structure engenders steric constraints on the relaxation from neighboring non-bonded segments. The severity of the intermolecular constraints on segmental relaxation can be related in a plausible fashion to the polymer's chemical structure; specifically, polymers with smoother, less polar, more compact, symmetric or flexible chain backbones and/or having less sterically hindering pendant groups experience weaker constraints on their segmental relaxation from interactions with neighboring, non-bonded segments. When amorphous, such polymers exhibit a near Arrhenius temperature dependence and close to Debye-like relaxation. Polymers having less flexible backbones and/or sterically hindering pendant groups exhibit broad segmental dispersions and temperature dependencies near the extreme fragile edge; these characteristics reflect segmental relaxation that is strongly intermolecularly cooperative. This correlation interprets the behavior in terms of steric effects and backbone structure; no recourse to free volume considerations is necessary. The data for polymers parallel observations made on small molecule glass-forming liquids, whose chemical structure similarly governs the strength of the intermolecular coupling, and thus the time and temperature dependence of segmental relaxation.

1. Introduction

It is obvious that segmental relaxation, involving localized motion of several backbone bonds, must depend in some manner on the local molecular structure. There have been a number of efforts to characterize this relationship [1-5]. Given the complexity of dynamics in dense phase, this is a non-trivial problem. The mechanism for segmental relaxation involves skeletal bond

rotations, with motion over large scales avoided by cooperative rotations of neighboring units along the chain. This intramolecular cooperativity gives rise to a segmental relaxation function having the Hall-Helfand [6,7] or similar [8,9] form. Polymers in dense phase have their motion further restricted by intermolecular cooperativity [10-15]. At times sufficient for intermolecular interactions to manifest themselves, the motion of a segment becomes coupled to those of neighboring, non-bonded species. This retards the relaxation, to an extent dependent on the strength of the intermolecular constraints.

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In this paper we present segmental relaxation data on a variety of polymers, both amorphous and semi-crystalline, intended to demonstrate a relationship between chemical structure and relaxation behavior. Specifically, it will be shown that there is less constraint on segmental relaxation from interactions with neighboring, non-bonded segments in polymers with smoother, less polar, more compact, symmetric or flexible chain backbones and/or having less sterically hindering pendant groups. This correlation of intermolecular cooperativity with chemical structure has been demonstrated previously for polybutadienes [16] and epoxidized polyisoprenes [17]. The strength of the intermolecular coupling is deduced from the normalized temperature dependence of the segmental relaxation time, and also, for amorphous polymers, from the spectral width of the segmental relaxation dispersion. Using this approach, the present study provides an interpretation of how chemical structure governs the magnitude of n (or the Kohlrausch-Williams-Watts (KWW) stretch exponent, $1-n$)

2. Theoretical background

2.1. Coupling model of relaxation

The coupling model, when applied to local segmental motion, is a homogeneous relaxation theory (i.e., all basic units are relaxing in the same manner at the same time). Of course, a distribution of relaxation times exists on a molecular level; however, the coupling model addresses relaxation of *macroscopic* variables (e.g., stress, dielectric polarization, density fluctuation, mean-square-displacement, enthalpy, etc.) [16]. An *average* has been performed over the basic relaxing units, such as the segments of polymers chains. The predictions of the model are concerned with *macroscopic* variables, notwithstanding the dynamic heterogeneous nature of relaxation at the *microscopic* level, as seen when the experimental probe monitors different subsets of the totality of the basic relaxing units (for example, as seen by 3d-NMR [18,19]).

When the relaxing units are dense packed and mutually interacting, all cannot move (e.g. reorient) in the same manner at the same time; this is

either impossible or very inefficient. Intermolecular constraints thwart some of the attempted conformation transitions, giving rise to random variations in the success rate for transitions by individual segments. Hence, at any given time, the motions of individual segments are not identical nor do they proceed homogeneously. The interaction and correlation among the relaxing units slows down on the average the individual relaxation rate.

According to the coupling model of relaxation [10–13,20], for neat polymers at the times appropriate for most experimental measurements, the slowing down of segmental relaxation gives rise to a correlation function having the KWW form [21, 22]

$$E(t) = E(0) \exp[-(t/\tau^*)^{1-n}]. \quad (1)$$

The temperature-dependent relaxation time, τ^* , is given by [10–13]

$$\tau^* = ([1 - n]\omega_c^n \tau_0)^{1/(1-n)}, \quad (2)$$

where τ_0 is the uncoupled (not intermolecular cooperative) relaxation time. It can be identified with one of the Hall–Helfand (intramolecularly correlated) relaxation times [17,23]. Recent quasi-elastic neutron scattering experiments [24], as well as molecular dynamics simulations [25] have confirmed the existence of a temperature-independent crossover time, ω_c^{-1} in Eq. (2), at which segmental relaxation assumes the KWW form. The parameter n , characterizing the degree of non-exponentiality of the relaxation function or the spectral width of the corresponding dispersion, is a measure of the strength of the intermolecular constraints on segmental relaxation. The value of this parameter ($0 \leq n < 1$) for a given species must depend on molecular structure because the latter ultimately determines the intermolecular interactions. However, the complexity of cooperative dynamics in dense liquids and polymers precludes direct calculation; n must be deduced from experiment.

From Eq. (2) it is seen that any temperature dependence of τ_0 , pertaining to conformational transition rates of an isolated chain, will be amplified in dense phase by the $1/(1-n)$ power. This means

that the temperature dependence of segmental relaxation observed for a neat polymer will parallel the magnitude of its coupling parameter [26–28]. Thus, the experimentally observed correlation between time and temperature dependencies [16,17, 23,26–34] is predicted by the coupling model of relaxation.

2.2. Cooperativity (fragility) plots

Over the range of most experimental measurements, temperature dependencies are non-Arrhenius; consequently, some normalization scheme must be invoked to allow comparisons among different fluids of the effect of temperature on the measured relaxation times. A plot of the relaxation time or transport coefficient versus T_g -scaled temperature was first introduced by Laughlin and Uhlmann [35] and exploited by Angell [29,30], who interpreted the sensitivity of the scaled temperature variation in terms of either the degradation of the structure with temperature (fragility) or the nature of a multi dimensional free energy hypersurface. For this reason, semi-logarithmic depictions of τ versus T_g/T are customarily referred to as fragility plots. We have suggested [16] a more appropriate name, at least for polymers, is the cooperativity plot. For segmental relaxation, the glass transition temperature can be operationally defined as the temperature at which the relaxation time assumes some arbitrary value. For dielectric results, usually carried out at relatively high frequencies, 1 s is a common reference point.

The validity of T_g -scaled Arrhenius plots of segmental relaxation times for glass-forming liquids can be assessed by comparing the results on polymers differing only in molecular weight [23]. Differences in molecular weight result in identical segmental relaxation functions (or dispersions) which occur, however, at different times and temperatures. When relaxation times obtained at different temperatures for polymers differing only in molecular weight are plotted in the $\log \tau$ versus T_g/T form, a single relation is obtained [23]. This verifies this normalization scheme as a rational means to classify and distinguish the segmental relaxation characteristics of polymers.

2.3. Segmental relaxation in semi-crystalline polymers

Many polymers, especially those having simple chemical structures and hence weak intermolecular coupling, are semi-crystalline. Crystallization broadens the segmental relaxation dispersion and shifts it to lower frequencies [36–39]. This indicates that amorphous chain segments in proximity to the crystalline phase have their motions restricted by the latter. The dispersion no longer has the KWW form (Eq. (1)), precluding determination of n by direct fitting. In a recent work [40] we demonstrated that crystallinity has an insignificant effect on the measured temperature dependence of the segmental relaxation time, at least when the temperature is normalized by the glass transition temperature, T_g , of the polymer. We interpret this as indicating that the primary effect of crystallinity is to introduce a different environment to those segments residing near to the crystalline phase. Such segments have their motions further retarded, thus broadening (inhomogeneously) the relaxation. The dominant contribution to the observed relaxation comes from segments far from crystallites, and hence relaxing in a similar fashion to that seen in the amorphous state. Since the temperature dependence of the relaxation still reflects these segments, it is their degree of intermolecular cooperativity which governs the temperature dependence of the relaxation time. The correlation of intermolecular coupling strength is retained [40]. Thus, while the shape of the segmental relaxation function is altered by crystallinity, the normalized temperature dependence of the segmental relaxation time is not. It can be used, therefore, to assess the correlation between structure and intermolecular coupling strength in semi-crystalline polymers.

3. Results

In this paper we are primarily concerned with intermolecular cooperativity arising from steric interferences. We restrict our comparisons primarily to pairs or groups of polymers for which the intermolecular potentials are similar in nature. Obviously, the magnitude of the intermolecular forces

Table 1.
Summary of segmental relaxation results

		T_g^a	n^b	T/T_g sensitivity	
Polyethers	POM	183	—		
	PTHF	178	0.40 ^c		
	PAA	253	0.47	Increasing	Fig. 1
	PPO	205	0.51		
Polyvinyl esters	PVAc	318	0.41		
	PVBz	359	0.46	Increasing	Fig. 2
Polymethylene backbone	PE	198 ^c	—		
	PVME	256	0.52		
	PVE	271	0.59	Increasing	Fig. 3
	PVC	—	0.77		
Aromatic polyesters	PET	353	0.52		
	BPA-PC	419	0.64	Increasing	Fig. 4

^aDefined to be the temperature at which the dielectric relaxation time equals 1 s.

^bUncertainty is typically ± 0.02 or better.

^cDetermined from quasi-elastic neutron scattering data.

(arising from London dispersion forces, polar interactions, hydrogen bonding, complex formation, etc.) will also influence the segmental dynamics. The comparisons, listed in Table 1, are illustrated in Fig. 1-5. In every case for which the coupling parameter can be determined by fitting the segmental relaxation dispersion in the dielectric loss, a larger n is associated with a stronger T_g -scaled temperature dependence. Both properties reflect more severe constraints on the relaxation from intermolecular interaction.

4. Discussion

4.1. Polyethers

In Fig. 1 dielectric relaxation results are given for polyoxymethylene (POM), polytetrahydrofuran (PTHF), polyacetaldehyde (PAA), and polypropylene oxide (PPO). The chemical structure, illustrated in the figure, effects subtle differences in both chain flexibility and transverse chain dimensions. The free rotation about the ether linkage confers

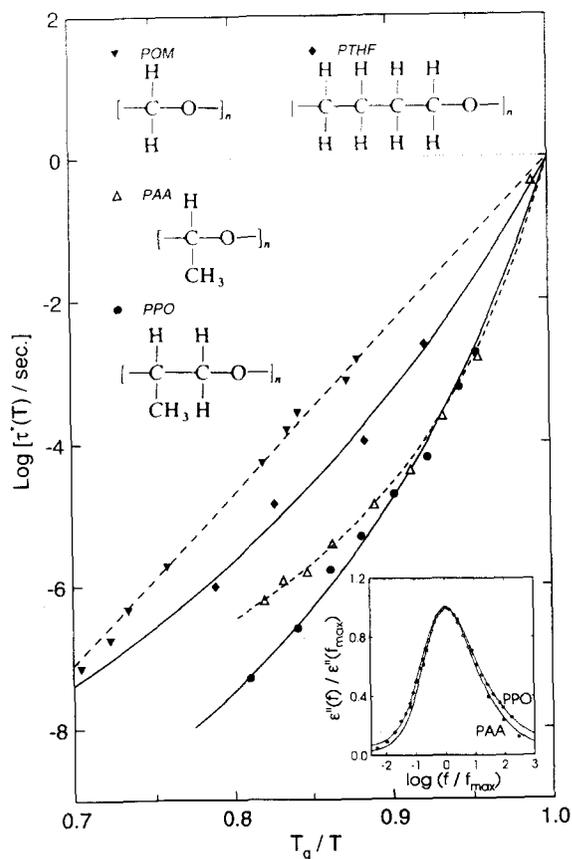


Fig. 1. The segmental relaxation time as a function T_g -normalized temperature for polyoxymethylene, polytetrahydrofuran, polyacetaldehyde and polypropylene oxide. The inset shows the corresponding dispersions in the dielectric loss spectrum for the two amorphous polymers, PPO and PAA. Except where otherwise noted, in this and other figures, the segmental relaxation time, τ^* , is defined to equal $(2\pi f_{\max})^{-1}$, where f_{\max} is the frequency of the peak maximum, while T_g is the temperature at which $\tau^* = 1$ s.

flexibility; however, the rotational freedom of the chain units is to an extent contravened by any backbone C-C bonds. The latter enhance intermolecular coupling because some opportunities for relaxation cannot be taken advantage by a stiffer chain. In addition, the presence of pendant methyl groups on the backbone carbons will tend to impede relaxation by virtue of steric interferences among non-bonded neighboring segments. These considerations might suggest that the strength of intermolecular coupling among the four polyethers

in Fig. 1 will vary as

POM < PAA < PTHF < PPO.

The T_g -normalized temperature dependences of the respective segmental relaxation times of these polymers (Fig. 1) indicate that the strength of intermolecular coupling increases in this manner (see Table 1).

Since PPO and PAA are amorphous, the shape of the dispersion in the dielectric loss can be used to deduce n (Eq. (1)), and hence quantify the relative magnitudes of the intermolecular coupling strengths. This is not the case for the semi-crystalline POM and PTHF, whose dispersions are inhomogeneously broadened whereby the shape is no longer reflective of intermolecular cooperativity. However, quasielastic neutron scattering data obtained on PTHF [41-43] yields a value for the coupling parameter. The values of n available for the three polymers, PPO, PPA, and PTHF, are listed in Table 1, and corroborate the relative degrees of intermolecular cooperativity suggested above.

4.2. Polyvinyl esters

Polyvinyl acetate (PVAc) and polyvinyl benzoate (PVBz) have similar chemical structures (Fig. 2); however, the bulkier side group of PVBz is expected to effect stronger intermolecular cooperativity than in PVAc. Fitting the dielectric loss spectra of the two polymers to Eq (1) reveals that indeed $n_{PVAc} < n_{PVBz}$ (Table 1). Consistent with this result, PVAc has a weaker T_g -normalized temperature dependence of its segmental relaxation time (Fig. 2). Hence, both the shapes and temperature dependences are consistent with stronger coupling in the bulkier polyvinyl ester.

4.3. Polymers with polyethylene backbone

The intermolecular coupling strength of linear polyethylene (PE) can be compared to that of polymers with the same backbone atoms, but different pendant groups (see Fig.3). The latter are expected to promote mutual interferences during relaxation of neighbor segments. Poly (vinylethylene) (PVE) has a simple backbone like polyethylene, but on

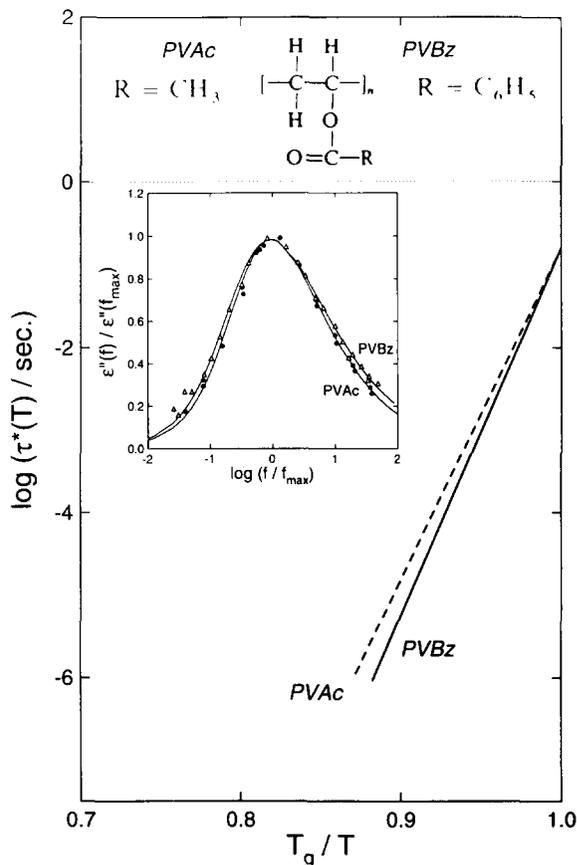


Fig. 2. Cooperativity plots for polyvinyl acetate and polyvinyl benzoate, along with the corresponding segmental relaxation dispersions. Due to the limited data available, T_g (= 318 and 359 K for PVAc and PVBz, respectively) in this figure only is taken to be the temperature at which $f_{max} = 1$ Hz.

every other skeletal carbon there is a pendant vinyl moiety. These relatively inflexible vinyl carbons project over 3 Å from the chain backbone, and thus sweep out a large volume during the course of conformational transitions. The segmental relaxation of polyvinylchloride (PVC) [24] should be subject to steric effects arising from the pendant chlorine atoms, as well as the enhanced intermolecular interactions associated with their polarity. Polyvinylmethylether (PVME) [44] has a pendant moiety which is more flexible than that of PVE or PVC, leading to intermolecular cooperativity intermediate in strength between those polymers and PE. Hence, we anticipate the

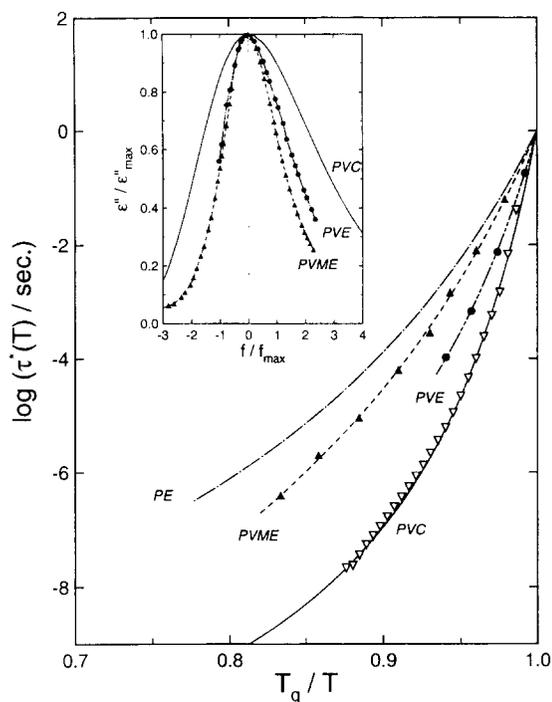


Fig. 3. Cooperativity plots for polyethylene, polyvinylchloride, polyvinylmethylether and poly(vinylethylene). Since the latter two polymers are amorphous, their segmental dispersions can be interpreted in terms of intermolecular coupling strength.

intermolecular coupling to vary as

$$PE < PVME < PVE < PVC.$$

Fig. 3 shows that the steepness of the T_g -scaled temperature dependancies of the four polymers rank orders in a manner consistent with these inferences drawn from the chemical structures. These results are also confirmed by fitting the dielectric data on PVE and PVME (Fig. 3) to eq (1), which yields $n_{PVME} = 0.52$ and $n_{PVE} = 0.59$. We also note that the dispersion of the PVC is very broad ($n_{PVC} = 0.77$). While this is consistent with strong intermolecular coupling, residual crystallinity may be contributing. In addition, in random copolymers the possibility exists for inhomogeneous broadening arising from the chemical heterogeneity of the backbone segments, with correspondingly different conformational transition rates (apart from inter-

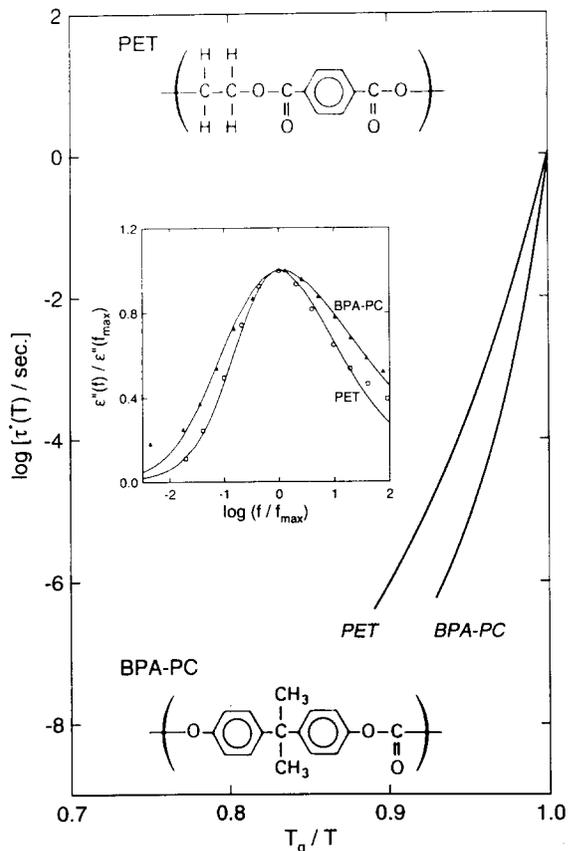


Fig. 4. The cooperativity plots and segmental dispersions for polycarbonate synthesized from bisphenol-A ($T_g = 419$ K) and for poly(ethylene terephthalate) ($T_g = 353$ K).

molecular cooperativity effects). This aspect of the relaxation dynamics of polymers is currently being investigated.

4.4. Polyesters

Polycarbonates synthesized from bisphenol-A (BPA-PC) have bulkier and less flexible chain units (Fig. 5) in comparison to all the polymers discussed so far. Based on this difference in molecular structure, we may conclude that its coupling parameter, n_{PC} , is larger than any of the coupling parameters of the polymers considered above, and also that the T_g -scaled temperature dependence of its relaxation time is considerably stronger. These predictions are verified by the dielectric data of

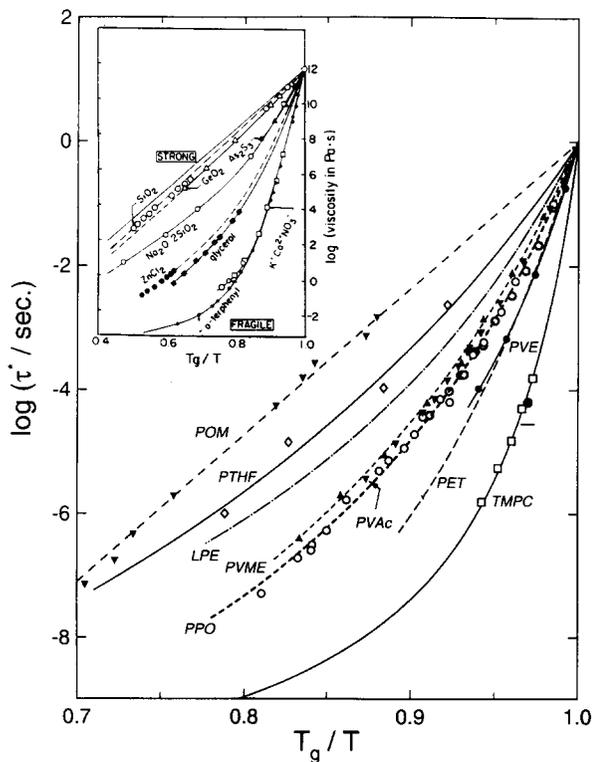


Fig. 5. Cooperativity plots for a variety of polymers, representing the extremes from strong intermolecular coupling to almost Arrhenius behavior. The inset shows the original T_g -scaled plots of shear viscosity of Angell [29,30] for small molecular and network glass-forming liquids.

BPA polycarbonate [45,46] and tetramethyl polycarbonate (TMPC) [34]. A more interesting comparison with BPA-PC is poly(ethylene terephthalate) (PET), whose respective chain units bear some resemblance to each other (Fig. 5). The essential difference is the additional phenyl ring in BPA-PC replacing the more flexible and compact ethylene unit in PET. Naturally, we then expect stronger intermolecular coupling in BPA-PC and the closely related TMPC than in PET. BPA-PC is amorphous and PET can be quenched into the amorphous state. From fitting the dielectric loss data of BPA-PC [45,46] and amorphous PET [39] we find that $n_{PC} = 0.64$ and $n_{PET} = 0.52$. The T_g -scaled temperature dependence of the relaxation time for BPA-PC and PET (Fig. 4) reveals the

stronger variation for BPA-PC than for PET, consistent with $n_{PC} > n_{PET}$.

5. Conclusions

The examples above, contrasting polymers of similar chemical structure, are consistent with a correlation between chain structure (flexibility, steric hindrance, compactness, smoothness and symmetry of the backbone and similar considerations for any pendant groups) and the degree of intermolecular cooperativity of the segmental relaxation. To see a much larger variation in cooperativity plots, in Fig. 5 we combine the data for a number of polymers, recognizing that since their chemical structures are of different classes, intramolecular cooperativity may intrude on the observed correlation. It is seen that the T_g -scaled temperature dependencies now vary greatly, increasing from the weak and almost Arrhenius behavior of the simplest polyoxide, POM, and the simplest hydrocarbon, PE, to the strongest dependence exhibited by the polycarbonates.

In an inset of Fig. 5 we show Angell's original T_g -scaled plot of shear viscosity of small molecular and network glass-forming liquids [29]. By comparing this inset with the main result for the polymers, we can conclude that the pattern seen for small molecular and network glass-forming liquids are reproduced in polymers, both amorphous or semi-crystalline. The limiting Arrhenius behavior seen in SiO_2 and GeO_2 for non-polymeric glass-forming liquids is recaptured for the polymer systems by the oxide polymers. On the other hand, polymers such as BPA-PC and TMPC have temperature dependences stronger than any of the small molecule liquids.

It is difficult to use comparisons of chemical structure to predict changes in intermolecular coupling for all the glass-forming liquids shown in the inset of Fig. 5. These materials range from inorganic networks, molten salts and small molecular van der Waal liquids. Meaningful comparisons can only be made if we restrict consideration to within some subclass of materials. In one study [47], limited to propylene glycol, 3-bromopentane and salol, it was found that the T_g -scaled tempera-

ture dependences of their dielectric relaxation times (obtained from published data [32,48]) indeed exhibited the expected correlation with intermolecular coupling inferred from the respective chemical structures. The coupling parameters, deduced by fitting the dielectric loss data, provided further corroboration [47].

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