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Structure-Dependent Enthalpy Relaxation at the Glass Transition of Polystyrenes[†]

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ABSTRACT: Parameters of Moynihan's model for enthalpy relaxation at the glass transition of polystyrene are shown to be sensitive to polymer weight, molecular weight distribution, and filler content, and a tentative structural explanation for the observed changes is proposed.

Introduction

According to a huge body of experimental evidence (e.g., ref 1–3), transition of a liquid substance into the glassy state (or vice versa) generally occurs over a more or less broad temperature interval, ΔT, and is accompanied by a characteristic change of principal thermodynamic variables (specific heat C, thermal expansion coefficient α, compressibility β, etc.). In most equilibrium theories of the glass transition it is implicitly assumed that $\Delta T = 0$, i.e., that change of the cited variables occurs in a jumplike fashion at a definite temperature T_g, which can thus be regarded as a "material constant" of a given substance.[4–6] On the other hand, kinetic theories concentrate on the analysis of the pattern of evolution of C, α, and β in the interval $\Delta T \neq 0$ as a function of thermal and mechanical prehistory.[7–11]

The theoretical basis of most current kinetic approaches is the assumption that during cooling at a constant rate, $q = \mathrm{d}T/\mathrm{d}t$, of the equilibrium liquid (i.e., melt) from a high temperature, $T_1 \gg T_g$, a moment is achieved when the rate of the structural rearrangements in the melt, which depends on thermal mobility of the molecules (or chain segments), starts to lag behind q. For this reason subsequent cooling of the sample will be accompanied by progressive deviation of its "instant" structure from the equilibrium one. Stated otherwise, at sufficiently low temperature, $T_2 < T_g$, a glassy substance will possess a "frozen-in" structure (or a set of structures) that the equilibrium melt would have at some "fictive" temperature, $T_2 < T_f \approx T_g$.

As shown by Moynihan,[13,14] temperature dependence of the structural parameter T_f may be described by

$$T_f(T) = T_1 + \int_{T_1}^{T}\left\{1 - \exp\left[-\left(\int_{T'}^{T}\mathrm{d}T''/q\tau\right)^{\beta}\right]\right\}\mathrm{d}T' \qquad (1)$$

where $\tau = A\exp[X\Delta h/RT + (1 - X)\Delta h/RT_f]$ is the relaxation time, Δh is the corresponding activation energy, $0 < X < 1$ is the nonlinearity parameter ($X = 1$ in the linear case), $0 < \beta < 1$ is the phenomenological measure of the width of the relaxation time spectrum ($\beta = 1$ for a single relaxation time), R is the gas constant, and A is a fitting constant.

Parameters entering eq 1 may be obtained by appropriate treatment of experimental observation of the evolution of a selected macroscopic property of a substance in the course of its cooling and heating. Having chosen relative enthalpy ΔH as a phenomenological characteristic of the structural state of a substance, one may calculate T_f, for example, at T_2 from the expression[13,14]

$$\Delta H(T_2) = \Delta H(T_f) - \int_{T_2}^{T_f}(\mathrm{d}\Delta H/\mathrm{d}T)_g\,\mathrm{d}T$$

which on account of a standard definition of specific heat, $C = \mathrm{d}\Delta H/\mathrm{d}T$, may be rewritten as

$$\int_{T_1}^{T_f}(C_1 - C_g)\,\mathrm{d}T' = \int_{T_1}^{T_2}(C - C_g)\,\mathrm{d}T'$$

Differentiation of the latter equation yields the following expression for the temperature coefficient of T_f:[13,14]

$$\frac{\mathrm{d}T_f}{\mathrm{d}T} = \frac{(C - C_g)|_T}{(C_1 - C_g)|_{T_f}} \qquad (2)$$

where C is the relaxation part of specific heat in the glass transition interval. Thus, one has to search for optimum values of parameters from eq 1 that would provide minimum deviation of the calculated curves of "reduced" (i.e., nondimensional) specific heat obtained by differentiation of eq 1 from corresponding experimental curves at the same cooling rate constructed from eq 2.

Recently, Hodge et al.[15,16] made an attempt to find correlations between the parameters $\Delta h/R$, X, and β and the molecular characteristics of a polymer. As will be shown below, numerical values of these parameters are also sensitive to structural changes of the same polymer pre-

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[†] Dedicated to Professor Dr. Josef Schurz on the occasion of his 60th birthday.

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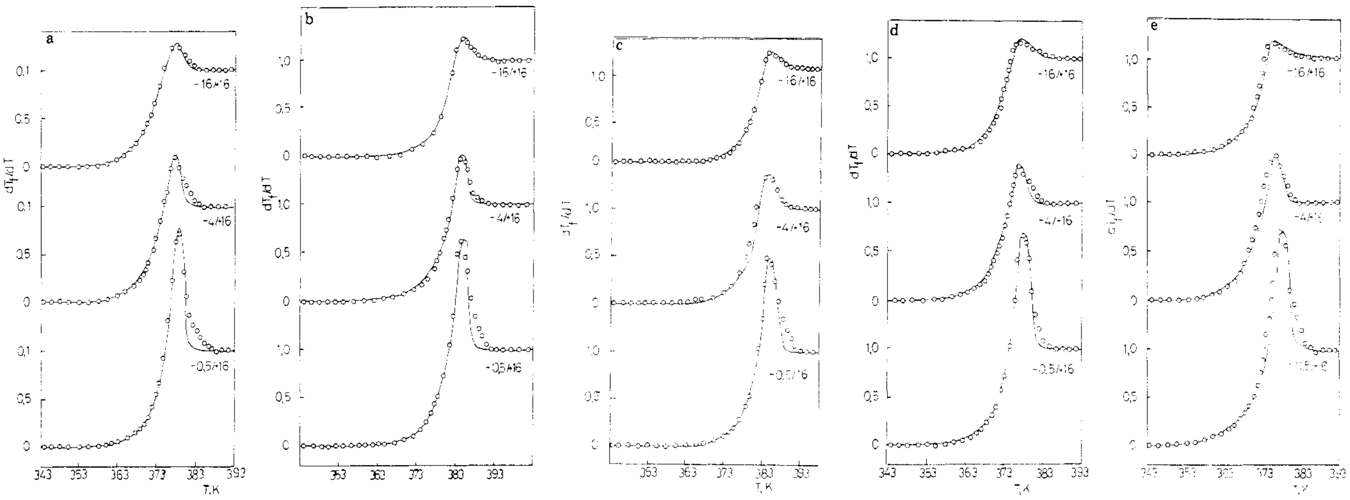

Figure 1. Experimental (points) and theoretical (full lines) dependences of dT_f/dT on T for n-PS-17 (a), n-PS-110 (b), n-PS-233 (c), w-PS-196 (d), and f-PS-196/50 (e). At each curve cooling and heating rates are shown by values (K/min) in numerator and denominator, respectively.

pared under a variety of experimental conditions.

Experimental Section

Samples. Narrow fractions ($\langle M_w \rangle / \langle M_n \rangle < 1.06$) of atactic polystyrene with molecular weights 9.0×10^3, 17.5×10^3, 110×10^3, and 233×10^3 (hereafter referred to as n-PS-9, n-PS-17, etc.) were provided by Professor T. Nose (Tokyo Institute of Technology).

An unfractionated sample of polystyrene (viscosity-average molecular weight $\langle M_v \rangle = 196 \times 10^3$) was provided by Dr. Ye. V. Lebedev (Institute of Macromolecular Chemistry, Kiev) and designated as w-PS-196.

Filled samples were prepared by careful mechanical mixing of powdery w-PS-196 with the necessary amount of inorganic glass powder (mean dimensions of particles about 2×10^{-6} m) at 298 K and subsequent hot pressing at 473 K and a pressure of 30–50 MPa. Filler content was 1, 20, 50, and 70 weight parts (samples f-PS-196/1, f-PS-196/20, etc.).

Calorimetry. Specific heat in the temperature interval 308–453 K was measured with the aid of a differential scanning calorimeter (Model DSM-2M). Each sample was kept in the calorimeter cell at 453 K for 5 min, cooled at one of six available constant cooling rates (from 0.5 to 16 K/min) to 308 K, and, after storage in isothermal conditions for 5 min, reheated at 16 K/min. The raw input data for calculation of specific heat from traces on the recorder chart were averaged from 4 or 5 independent measurements for each sample at each cooling rate and then presented as a two-dimensional set with parameters "temperature" and "cooling rate". Specific heats were then calculated on a digital computer, Model ES-1033, with the aid of a program providing interpolation based on observed positions and heights of relaxation peaks on specific heat curves, as well as junction points of peak slopes and linearly extrapolated lines C_l and C_g, which served to choose the discrete temperature steps ΔT_i (from 5 K in the linear ranges of specific heat curve to 1 K in the relaxation region). Relative uncertainty of derived specific heat values was well within 2.5%, and data from independent measurements were reproducible within the same limits.

Results and Discussion

Data Treatment. Treatment of the experimental data was basically similar to that described by Hodge,[15] so only essentials will be mentioned here. First, parameters describing linear temperature dependences of C_l and C_g were obtained by least squares, "final" values of T_f (at 308 K) were determined for each sample as a function of cooling rate q, and then values of $\Delta h/R$ were calculated by least squares with double precision (up to 15 significant numbers) from the expression[13]

$$d \ln |q| / d(1/T_f) \approx -\Delta h/R$$

Table I
Parameters of Enthalpic Relaxation

sample	$10^{-3}\Delta h/R$,[a] K	$\ln A$,[b] s	X	β
n-PS-9	76.1	198.8	0.400 ± 0.033	0.630 ± 0.025
n-PS-17	88.8	234.4	0.430 ± 0.030	0.530 ± 0.025
n-PS-110	101.0	263.0	0.420 ± 0.033	0.505 ± 0.015
n-PS-233	110.0	287.8	0.410 ± 0.033	0.468 ± 0.025
w-PS-196	80.5	211.6	0.480 ± 0.040	0.580 ± 0.025
f-PS-196/1	80.9	214.0	0.490 ± 0.020	0.500 ± 0.015
f-PS-196/20	84.0	223.4	0.480 ± 0.020	0.450 ± 0.010
f-PS-196/50	91.0	243.7	0.036 ± 0.020	0.430 ± 0.015
f-PS-196/70	98.0	260.8	0.028 ± 0.015	0.0380 ± 0.010

[a] ±10%. [b] ±0.8.

Optimum values of parameters X, β, and A for each cooling regime for each sample were automatically calculated on digital computers, Models ES-1033 and ES-1050, by the method of iterations with the aid of a program providing minimization of the mean square deviation between theoretical and experimental curves of dT_f/dT. The analyzed envelope was halved at each iteration step, so that at the seventh step it was well within 1% of desired accuracy. To save computer time, raw values of the fitting parameter A were estimated from the empirical relationship[17]

$$\ln A = -\Delta h/RT_p$$

where T_p is the temperature of the relaxation peak on the specific heat curve. The latter relationship is qualitatively consistent with a correlation between $\Delta h/R$ and $\ln A$, ensuing from the assumption τ = const.[16]

In Table I are listed the numerical values of kinetic parameters for enthalpic relaxation of the studied samples, which were obtained by averaging out corresponding individual values for each of 5 or 6 cooling regimes of each sample. We remark, in passing, that the relative uncertainties of the X and β values shown in the table are simply the deviations from the arithmetic mean of the individual values for 5 or 6 cooling regimes and not the standard deviations, which are of the order of 7–10% of a corresponding figure.

As can be seen from Figure 1, in which theoretical and experimental curves of dT_f/dT are compared for several samples, Moynihan's method permits a semiquantitative description of the observed patterns of the change of relaxation heat capacity of all samples studied in the glass transition region. (Deviations of experimental points from

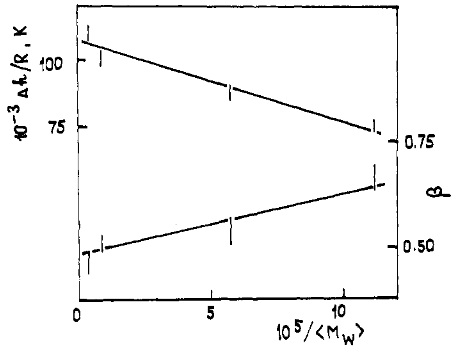

Figure 2. Dependence of parameters $\Delta h/R$ and β on $1/\langle M_w \rangle$ for narrow fractions of PS.

symmetric theoretical curves on the high-temperature side of the relaxation peak are obviously due to instrumental thermal lag.)

Effect of Molecular Weight. As can be seen from Table I, values of $\Delta h/R$ for narrow fractions of PS increase smoothly with molecular weight, which is a natural consequence of a correlation between $\Delta h/R$ and T_f and/or T_g.[8,18] Similar effects were reported by Petrie et al.[19] for polystyrene and by O'Reilly[20,21] for polystyrene and poly(vinyl chloride). The observed dependence of $\Delta h/R$ on $\langle M_w \rangle$ (Figure 2) was found to obey the empirical relationship

$$10^{-3}\Delta h/R\ (\mathrm{K}) = 107 - 2.88 \times 10^5/\langle M_w \rangle \qquad (3a)$$

although an approximately equally good fit may be shown to result from a different correlation

$$10^{-3}\Delta h/R\ (\mathrm{K}) = 20.2 \log \langle M_w \rangle \qquad (3b)$$

In contrast to the data of Petrie et al.[19] as analyzed by O'Reilly,[20] our values of X do not exhibit a measurable dependence on molecular weight (Table I). This disagreement is, however, not very frustrating, taking into consideration differences in sample history and the data treatment. For example, O'Reilly obtained $X = 0.40$ for a narrow PS fraction with $\langle M_w \rangle = 4 \times 10^3$, while for PS samples of essentially the same molecular weight from the work of Petrie et al. he derived $X = 0.28–0.29$.[20] Moreover, the reported values of X for poly(vinyl chloride) vary in the range from 0.2–0.3[21] to 0.11.[16] These examples show the obvious hazards of attempts to rationalize the experimental results from different laboratories in the framework of a unified, coherent picture.

As follows from our analysis, β decreases with rising $\langle M_w \rangle$ (Figure 2) according to the relationship

$$\beta = 0.47 + 1.34 \times 10^3/\langle M_w \rangle \qquad (4)$$

Correlation between parameters $\Delta h/R$ and β is evident from comparison of relationships 3a and 4, and may be approximated as $(\Delta h/R)\beta = (49 \pm 2) \times 10^3$ K. This result is consistent with Hodge's data,[16] but Hodge's observation of correlation between $\Delta h/R$ and X (or, equivalently, between β and X) does not hold for the narrow fractions of PS studied in this work.

A tendency of broadening of the enthalpic relaxation time spectrum in the glass transition region of PS with increasing molecular weight, which manifests itself as a regular decrease of relaxation parameter β, may be formally attributed to the onset of a new relaxation mechanism due to the appearance of new structural entities in higher members of the series. Apparently, the most likely candidates for these hypothetical structures would be topological entanglements, which appear in molten PS in the vicinity of a "critical" molecular weight $M_c = 33 \times 10^3$, as measurements of maximum Newtonian viscosity suggest.[22] However, an approximately linear pattern of dependence of β on $1/\langle M_w \rangle$ (Figure 2), as typical for an end-group effect, makes one believe that a more probable reason for the narrowing of the relaxation spectrum of lower members of the PS series might be the decrease of the degree of cooperativity of the relaxation process due to "dilution" of the continuous phase of contiguous chain segments by end groups. In other words, the appearance of structurally identical topological entanglements in high molecular weight PS does not result in a radical change of PS local structure on a scale at least comparable to dimensions of structural entities involved in enthalpy relaxation during glass transition (presumably, chain statistical segments). This conclusion agrees favorably with the experimentally observed invariance of the "structural" parameter X for all studied narrow fractions. Nevertheless, additional experiments on PS with molecular weights both below and above M_c are clearly needed for unequivocal judgment on the exact functional form of the dependence $\beta = f(\mathrm{MW})$.

Effect of Molecular Weight Distribution. It follows from the comparison of relaxation parameters for higher narrow fractions n-PS-110 and n-PS-233 with those for the unfractionated polymer w-PS-196 (Table I) that broadening of the molecular weight distribution leads to a lowering of the activation barrier for relaxation $\Delta h/R$ and to an increase of X and β. Considering the results of the above analysis for narrow fractions, it can be supposed that eased segmental mobility (lower $\Delta h/R$) and decreased cooperativity of relaxation process (increased β) reflect the effect of dilution of the continuous, higher molecular weight phase of w-PS-196 by lower molecular weight components. On the other hand, concomitant decrease of the degree of nonlinearity (higher X) suggests a possibility of the change of local PS structure brought about by lower homologues (e.g., as a result of the change of relative concentration of chain end groups in the immediate vicinity of entanglement network junctions).

Roughly similar patterns (i.e., decrease of $\Delta h/R$ and increase of both β and X with broadening molecular weight distribution) may be inferred from comparison of the data of Hodge et al.[15] and Chow et al.[10] for PS.

Effect of Filler. Analysis of the data for filled samples (Table I) reveals that activation energy $\Delta h/R$ increases while parameters X and β decrease with growing content of filler. These results, in conjunction with the data obtained in thermodynamic studies of the same systems in the melt,[23,24] suggest that the observed changes reflect the appearance of boundary layers of PS with changed structure near the filler surface. Thus, decrease of β may be attributed to a broadening of relaxation time spectra due to structural changes of PS trapped in boundary layers, whereas a simultaneous increase of $\Delta h/R$ and decrease of X may be caused by steric hindrances to structural relaxation in boundary layers. These phenomenological arguments are in complete agreement with the concept of enhancement of structural heterogeneity of the polymeric phase due to a solid surface, advocated for many years by one of the present authors.[25]

Conclusions

The results of the above analysis illustrate the applicability of Moynihan's model to a semiquantitative description of enthalpy relaxation at the glass transition of polystyrenes differing in structure and composition. To a considerable extent, our data confirm Hodge's finding of cross correlation between relaxation parameters A, $\Delta h/R$, X, and β.[15,16] However, of all the mentioned parameters, it is X that seems to provide the most objective information on polymer local structure in the studied system, since this parameter is least correlated to the other parameters of the model. In our opinion, Moynihan's approach is a valuable tool in the analysis of the effect of delicate differences in molecular or supermolecular structure on relaxation properties of heterogeneous polymeric materials.

Registry No. polystyrene (homopolymer), 9003-53-6.

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Polymer-Supported Catalysis: Stereoselective Oxidation of L-Dopa by Iron(III) Complex Ions Anchored to Asymmetric Polymers

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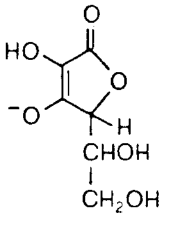
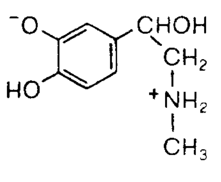
ABSTRACT: $[Fe(tetpy)(OH)_2]^+$ ions anchored to sodium poly(L-glutamate) or sodium poly(D-glutamate) were used as catalysts for the H_2O_2 oxidation of L-dopa at pH 7 (tetpy = 2,2′:6′,2″:6″,2‴-tetrapyridyl). The catalytic sequence involves (a) formation of a substrate–catalyst precursor complex, (b) intramolecular electron transfer within this intermediate, and (c) oxidation of both the lower valence metal chelate and dopa radical by H_2O_2 in subsequent fast steps. Stereoselective phenomena are observed only when the formation of the diastereomeric precursor complexes is assisted by the ordered polypeptide matrices. The conformational asymmetry of the polymers ensures different steric constraints for LL and DL adducts, which are thought to affect differently the mutual orientation and separation distance of the redox centers, in agreement with the finding that chiral discrimination is chiefly observed in step b. A hypothetical model of the diastereomeric noncovalent electron-transfer complexes was constructed by conformational energy calculations. The models are consistent with a number of experimental findings and support the hypothesis that stereoselectivity is coupled with a remote attack mechanism on the central metal ion. Implications of the stereochemical features of the catalytic systems on the efficiency of reaction are also discussed.

Introduction

Second-order rate constants of outer-sphere redox processes are expressible as products of the equilibrium quotient for the formation of a precursor complex (K_0, M^{-1}) and the unimolecular specific rate for the electron-transfer step (k_{et}, s^{-1}), when this latter is rate-determining.[1] In a very few cases, however, it has been proved possible to resolve the observed rate constants into their elementary components,[2,3] because no saturation kinetics are often observable.[1b] Furthermore, in all but few instances[4,5] redox reactions between pairs of achiral species have been studied, despite the fact that the use of optically active compounds could have some relevance for biological processes as well as for practical purposes.



(I)



(II)

We have recently shown that the H_2O_2 oxidation of L(+)-ascorbic acid (I) and L-adrenaline (II) catalyzed by hemin-like $[Fe(tetpy)(OH)_2]^+$ ions (tetpy = 2,2′:6′,2″:6″,2‴-tetrapyridyl) anchored[6] to sodium poly(L-glutamate) (FeTL) or sodium poly(D-glutamate) (FeTD) proceeds stereoselectively only when the formation of the diastereomeric precursor complexes is assisted by the ordered polymeric matrices.[7] Stereoselectivity ratios (k_{DL}/k_{LL}) around 4 were then obtained, corresponding to an enantiomeric excess of about 65%. Moreover, kinetic data in the steady-state conditions allowed us to evaluate k_{et} and K_0,[7b,c] and the product $k_{et}K_0$ was found to be in

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