

# Flexibility and Phase Transitions of Polymers

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**ABSTRACT:** It is shown, that both the mobility of polymers as well their transition temperatures (glass transition and crystallization) depend on the "flexibility" of simple bonds, i.e., on their ability to promote by energetically stimulated rotations conformational changes to release stresses. The polymer class specific interdependence between melting temperature,  $T_m$  and glass temperature,  $T_g$ , suggests that the "flexibility" of polymers depends additionally on the probability of interactions between sequences of polymer chains. Interaction between polymer chain sequences controls at the same time the ordering necessary for crystallization. Char-

acteristic of polymers is thus the dependence of both transition temperatures on the "mass/flexible bond" of the monomeric (repeating) unit,  $\mu/\rho$ . This experimentally observed polymer class specific behavior is reflecting the similar probabilities of interaction within a given class of polymers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1590–1599, 2003

**Key words:** glass transition; melting point; structure-property relations; phase transitions

## INTRODUCTION

In contrast to simple molecules where mobility is controlled by energetically induced changes of the spatial distribution, thus affecting the combinatorial entropy of the system, polymer mobility depends essentially on the possibility of conformational rearrangements to release energy induced stresses, implying consequently changes of the conformational entropy. That means if force is applied the polymer chain attempts to release induced stresses by conformational changes, i.e., by readjusting its conformation to relieve the stress.<sup>1</sup> Taking into account the very large number of monomeric units connected in polymer chains, conformational rearrangements depend first of all on intramolecular cooperativity and "flexibility" of the individual connected monomeric units. As the smallest polymer unit of rotation (the so called "conformer") is surrounded by other conformers, any relaxation by rearrangement of the energetically excited conformation imposes rotations around the connecting simple bonds implying at the same time cooperative motions of all surrounding neighbors. That means, however, that any conformational change causes not only conformational entropy changes but also calls for the necessary energetic contributions to overcome rotational barriers for allowing rotations

around simple bonds. Conformational entropy will consequently drop rapidly with decreasing temperature to reach its "equilibrium zero value," i.e., the so-called "zero conformational entropy temperature,"  $T_0$ , characterizing a real thermodynamic second-order transition. It is assumed that the second-order transition is identical with the so-called "Vogel temperature"<sup>2</sup> situated well above  $0\text{K}$ .<sup>3,4</sup> This assumption of vanishing conformational entropy at  $T_0$  also allowed the explanation of the "Kauzmann paradox."<sup>5</sup>

As a result of the kinetic character of relaxation processes within polymers and of the belonging conformational changes, polymer mobility "freezes in" well above this equilibrium temperature,  $T_0$ , at the on-operational conditions ("cooling/heating rate" and "frequency") dependent "glass transition temperature,"  $T_g$ , which shows the characteristics of a thermodynamic "second-order transition," i.e., discontinuities of the second-order derivatives of the "Gibbs energy." The temperature at which the second-order transition,  $T_0$ , occurs may be estimated using the WLF equation. Generally it is assumed that the second-order phase transition will be observed at about  $50^\circ\text{C}$  below  $T_g$ , i.e.,  $T_g = T_0 + 50\text{K}$ .<sup>3,6</sup>

Concerning the "glass temperature,"  $T_g$ , Schneider and DiMarzio<sup>7</sup> have shown that in a first approximation  $T_g$  can be correlated with the ratio mass/"flexible bond" of the monomeric unit,  $\mu/\rho$  (which essentially controls the possibility of conformational changes).

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$$T_g = C \mu/\rho \quad (1)$$

Later it has been shown that  $C$  is not an universal constant as initially supposed, but rather a polymer class-specific constant.<sup>8</sup> The scatter of the data is of the same order as observed for other semiempirical methods recommend for predicting the glass temperature of polymers using chemical structure increments and specific properties of the polymers (density or specific volume)<sup>9</sup> respective mass moments and conformational flexibility (evaluated in terms of torsion angle units).<sup>10</sup> The correlation coefficient of these attempts of correlating  $T_g$  with properties of polymers is generally in the range of about 0.90.

Taking into account the effect of possible interactions and steric hindrances on rotations around simple chemical bonds a reliable determination of an exact number of "flexible bonds" of the monomeric unit remains, however, ambiguous. Accounting for possible interactions and steric hindrances it is also unlikely that the number of "flexible bonds" of the monomeric unit will be an entire number, equal with the number of simple bonds of the monomeric unit. It may, hence, be supposed that the Schneider-DiMarzio rule holds, as suggested only within the different classes of polymers of similar chemical structure, due to alike effects of interactions and steric hindrances.

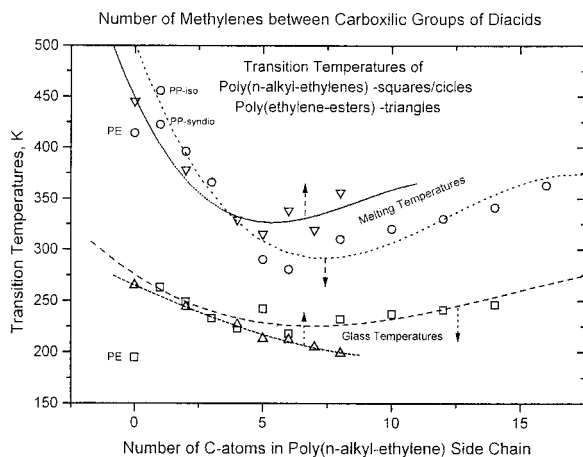
Considering the melting temperature of polymers,  $T_m$ , Simha and Boyer<sup>11</sup> suggested the existence of an universal empirical correlation between  $T_m$  and  $T_g$ .

$$T_m = aT_g + b \quad (2)$$

Boyer<sup>12</sup> has subsequently emphasized that depending on the polymer structure  $T_m = 2T_g$  for polymers of symmetrical structure and  $T_m = 1.4T_g$  for unsymmetrical polymers. These empirical correlations were later supported by the statement that both glass and melting temperature are dependent on the cohesive energy density (CED) and chain stiffness,<sup>13</sup> which, in fact, both control conformational changes.

As an additional support for the similar influences of regular changes within the chemical structure of polymers on glass and melting temperature in Figure 1, the influence of an increasing number of methylenes in the side chain substituents of poly( $n$ -alkyl ethylenes) and between the carboxylic groups of the diacids in the main chain of poly(ethylene-esters) is exhibited. It is interesting to notice that at the beginning the increasing mobility of the polymers with increasing number of "flexible" methylenes causes a decrease of both glass and melting temperature showing a minimum value for about five to six methylenes substituted in both the alkylic side chain of poly( $n$ -alkyl ethylenes) and the main chain of poly(ethylene-esters).

The decrease of the glass temperature with increasing number of  $\text{CH}_2$  units of the alkyl spacer in polymeric side chains has been observed for other polymer



**Figure 1** Influence of the length of methylenic spacer, expressed by the number of C-atoms, on the transition temperatures of poly( $n$ -alkyl ethylenes) and poly(ethylene-esters) of diacids.

classes also.<sup>14</sup> This decrease of the glass temperature with increasing length of the side chain has been attributed to plastisizer effects of the mobile methylenic units.<sup>15</sup> For a higher number of methylenes, however, the transition temperatures increase again, suggesting a decrease of the mobility of the neighboring methylenes.

Concerning the decrease of the mobility reflected in an increase of the glass temperature of poly( $n$ -alkyl ethylenes) bearing longer methylenic side chains, it has been assumed that crystallization of the side chains it self is occurring, due to an increased order of the longer  $n$ -alkylic units.

An other possible explanation could be that an increased probability of a crankshaft like arrangement within longer methylenic units promotes independent motions of these crankshaft conformations detrimental to the "flexibility" of the individual methylenes within crankshafts, consequently reducing the overall mobility of the repeating unit.

Assuming that the overall melting entropy of polymers,  $\Delta S_u$ , is larger as the change in conformational entropy at the melting temperature,  $\Delta S_c$ , because it includes the increase in entropy from  $T_0$  to the rotational isomeric state at  $T_m$

$$\Delta S_u = \Delta S_c [T_m / (T_m - T_0)] \quad (3)$$

Matsuoka<sup>16</sup> has shown that the correlation between glass and melting temperature of polymers may be expressed as

$$T_g/T_m = 0.5 + 50/T_m \quad (4)$$

According to this correlation the ratio of  $T_g/T_m$  is  $2/3$  for low melting polymers with  $T_m$  near 273 K and  $1/2$  for higher melting polymers.

**TABLE I**  
**Transition Temperatures of Polymers (Polymer Handbook) and Mass/"flexible Bonds" of Monomeric Unit**

Polymer	$T_g, K^a$	$T_m, K^a$	$\mu/\rho$
<i>Poly(n-alkyl-ethylenes)</i>			
Polyethylene	0 <sup>b</sup>	195 ( $\pm 10$ ) <sup>c</sup>	414 ( $\pm 4$ )
Poly(methylmethylenes), i.e., Poly(propylene)	1	263 ( $\pm 3$ )	iso 455.5 ( $\pm 17.5$ ) syndio 422.5 ( $\pm 11.5$ )
Poly(ethylene/1-butene)	2	249	396 ( $\pm 13$ )
Poly(propylene)	3	233	366 ( $\pm 18$ )
Poly(butylene)	4	223	218? <sup>d</sup>
Poly(pentylene)	5	242	290
Poly(hexylene)	6	218 ( $\pm 10$ )	280.5 ( $\pm 2.5$ )
Poly(octylene)	8	232	310 ( $\pm 3$ )
Poly(decylene)	10	237	320 ( $\pm 2$ )
Poly(dodecylene)	12	241	330
Poly(tetradecylene)	14	246	341
Poly(hexadecylene)	16	328? <sup>f</sup>	363 ( $\pm 10$ )
<i>Poly(styrenes), Poly(vinylpyridine), and poly(N-alkyl-3,6-carbazolylenes)</i>			
Poly(styrene)-iso		373	515.5 ( $\pm 7.5$ )
Poly(styrene)-syndio		382	543
Poly( <i>para-tert</i> -butylstyrene)		401.5 ( $\pm 2.5$ )	573
Poly( <i>para</i> -methylstyrene)		370 ( $\pm 4$ )	497
Poly( <i>meta</i> -methylstyrene)		370	488
Poly( <i>ortho</i> -methylstyrene)		409	633
Poly( <i>para</i> -fluoro-styrene)		368	538
Poly(2-vinyl-pyridine)		377	485
Poly(N-n-octyl-3,6-carbazolylene)			
$M_w = 2900$		333	405
$M_w = 10,000$		343	426
Poly(N-n-dodecyl-3,6-carbazolylene)		288	333
<i>Poly(ethylene-esters) and poly(alkyl-terephthalates) Poly(ethylene-esters)</i>			
Poly(ethylene-oxalate)	0 <sup>j</sup>	265	445
Poly(ethylene-succinate)	2	244	378.5 ( $\pm 2.5$ )
Poly(ethylene-adipate)	4	227	329 ( $\pm 9$ )
Poly(ethylene-pimelate)	5	213	305.5 ( $\pm 3.5$ )
Poly(ethylene-suberate)	6	212	338 ( $\pm 10$ )
Poly(ethylene-azelate)	7	205	319
Poly(ethylene-sebacate)	8	199	351 ( $\pm 5$ )
Poly(trimethylene-adipate)		214	315 ( $\pm 4$ )
Poly(tetramethylene-sebacate)		216	335 ( $\pm 5$ )
Poly(decamethylene-adipate)		217	350 ( $\pm 3$ )
<i>Poly(alkyl-terephthalates)</i>			
Poly(ethylene-terephthalate)		345.5 ( $\pm 12.5$ )	547.5 ( $\pm 9.5$ )
Poly(tetramethylene-terephthalate)		290	500.5 ( $\pm 6.5$ )
Poly(pentamethylene-terephthalate)		283	411 ( $\pm 4$ )
Poly(hexamethylene-terephthalate)		264	430.5 ( $\pm 3.5$ )
Poly(heptamethylene-terephthalate)		276	371
Poly(octamethylene-terephthalate)		318	405
Poly(nonamethylene-terephthalate)		270	363
Poly(decamethylene-terephthalate)		213	350 ( $\pm 3$ )
Poly(ethylene-isophthalate)		324	416 ?, 513
<i>Poly(oxydes) and poly(sulfides)</i>			
<i>Poly(oxydes)</i>			
Poly(methylene oxyde/formald)	1 <sup>i</sup>	263	471 ( $\pm 17$ )
Poly(ethylene oxyde)	2	232	343 ( $\pm 5$ )
Poly(trimethylene oxyde)	3	195	315 ( $\pm 8$ )
Poly(tetramethylene oxyde)	4	189	320.5 ( $\pm 11.5$ )
Poly(hexamethylene oxyde)	6	190	333 ( $\pm 2$ )
Poly(2-butene oxyde)		203	379 ( $\pm 6$ )
Poly(ethylidene oxyde/acetaldehyde)		243	438
Poly(oxypropylene)		198	346.5 ( $\pm 1.5$ )
Poly(epichlorohydrine)		252	392 ( $\pm 2$ )
Poly( <i>para</i> -phenylene oxyde)		358	553.5 ( $\pm 8.5$ )

TABLE I Continued

Polymer	$T_g$ , K <sup>a</sup>	$T_m$ , K <sup>a</sup>	$\mu/\rho$
<i>Poly(sulfides)</i>			
Poly(ethylene sulfide)	253	468 ( $\pm 5$ )	60/2.5
Poly(trimethylene sulfide)	228	354	74/3.5
Poly(para-phenylene sulfide)	370	573 ( $\pm 5$ )	108/3
Poly(ethylene disulfide)	246	403	92/4
<i>Poly(amides)</i>			
Poly(6-amino caproic acid)	366.5 ( $\pm 6.5$ )	539 ( $\pm 6$ )	129/3.5
Poly(hexamethylene adipamide)	330	558.5 ( $\pm 15.5$ )	246/10
Poly(heptamethylene adipamide)	325.5 ( $\pm 7.5$ )	523	260/11
Poly(decamethylene adipamide)	313	508 ( $\pm 5$ )	302/13
Poly(hexamethylene suberamid)	330	508.5 ( $\pm 8.5$ )	254/11
Poly(hexamethylene sebacamide)	323	477 ( $\pm 29$ )	282/12.5
Poly(decamethylene sebacamide)	326 ( $\pm 6$ )	483.5 ( $\pm 5.5$ )	338/15
Poly(para-phenylene sebacamide)	383	607	274/10
Poly(hexamethylene terephthalamide)	413	664	246/8
Poly(p-phenylene terephthalamide)	613	873	238/6
<i>Poly(vinyls), poly(vinylidenes), and poly(methacrylates)</i>			
Poly(vinylchloride)	362.5 ( $\pm 8.5$ )	515.5 ( $\pm 30.5$ )	62.5/1.5 <sup>n</sup>
Poly(vinylfluoride)	314	488 ( $\pm 15$ )	46/1.5
Poly(vinylidene chloride)	255	468 ( $\pm 5$ )	97/2.5
Poly(vinylidene fluoride)	233	452 ( $\pm 9$ )	64/2.5
Poly(vinyl alcohol)	358	520.5 ( $\pm 19.5$ )	44/1.25
Poly(vinyl acetate)	305	448	86/3
Poly(acrylonitrile)	384 ( $\pm 14$ )	602 ( $\pm 18$ )	53/1.25
Poly(methacrylonitrile)	393	523	67/1.5
Poly(isopropyl acrylamide)	380.5 ( $\pm 22.5$ )	473	113/3.5
Poly(methyl methacrylate)-iso	311	463 ( $\pm 30$ )	100/3.5
-syndio	378	473	100/3
Poly(octadecyl methacrylate)	173	309	338/20
<i>Poly(dienes)</i>			
Poly(butadiene)- <i>cis</i>	167.5 ( $\pm 3.5$ )	285	54/3 <sup>o</sup>
- <i>trans</i>	215	370.5 ( $\pm 2.5$ )	54/2.5
Poly(1-ethyl-1-butenylene/hexadiene)	197	355	82/4
Poly(1-propyl-1-butenylene/heptad.)	196	358	96/5
Poly(1-butyl-1-butenylene/octadiene)	192	360	110/5.5
Poly(1- <i>tert</i> -butyl-1-butenylene)	293	379	110/4
Poly(2-methyl-1-butenylene)			
Poly(isoprene)- <i>cis</i>	212 ( $\pm 6$ )	305 ( $\pm 4$ )	68/3
- <i>trans</i>	207	345.5 ( $\pm 7.5$ )	68/3
Poly(1-chloro-1-butenylene)			
Poly(chloroprene)- <i>cis</i>	253	343	88.5/3.5
- <i>trans</i>	233	366.5 ( $\pm 13.5$ )	88.5/3.5

<sup>a</sup> Are given mean values together with the limits between which oscillate in literature presented conflicting transition temperature data.

<sup>b</sup> Number of side-chain C-atoms of poly(*n*-alkyl ethylene).

<sup>c</sup> Most probable value, see R.F. Boyer.<sup>20</sup>

<sup>d</sup>  $T_m < T_g$ ?, inconsistency of data listed in literature.

<sup>e</sup> Are assumed crankshaft motions of at least six adjacent methylenes, reducing the "flexibility" of the individual simple bonds in the longer *n*-alkylic units

<sup>f</sup> Accordingly to literature may be first-order transition.

<sup>g</sup> Are assumed in or out of plane conformations of stiff aromatic rings disposed along the main chain

<sup>h</sup> Supposing conformational identity of three -CH<sub>3</sub> groups attached to the same C-atom

<sup>i</sup> "Flexibility" of *ortho*-substituent may be hindered compared to the mobility of *para*-substituents.

<sup>j</sup> Number of methylenes between the carboxylic groups of diacids resp. the oxygens of poly(oxydes).

<sup>k</sup> Interaction between the oxygens of carboxylic groups may reduce their overall "flexibility"

<sup>l</sup> Due to the smaller probability of  $\pi$ - $\pi$  electronic interaction between phenyl and carboxylic groups the mobility of carboxylic substituents in the *meta*-position may be higher than in the *para*-position.

<sup>m</sup> Hydrogen bonding may reduce the mobility of linear poly(*n*-alkyl oxydes/sulfides).

<sup>n</sup> Inter- and intramolecular hydrogen bonding will reduce the "flexibility" of simple bonds in poly(vinyls). The increased probability of hydrogen bonding above all in PVC, poly(vinyl alcohol) and PAN is confirmed by the course of the thermal degradation (elimination of volatile HX molecules, without affecting the -C-C- chain backbone).<sup>21</sup>

<sup>o</sup> The higher probability of crankshaft-like motion increases the mobility of *cis*-compared to *trans*-sequences.

Using the data listed in Table I, in Figure 2 the dependencies of the  $T_g/T_m$  ratio on the melting temperature,  $T_m$ , are exhibited according to eq. (4) for the different polymer classes. The results are that the scatter of the data is extremely large, mainly in the lower temperature range. Nevertheless, for poly(*n*-alkyl ethylenes) and poly(styrenes/vinylpyridines/*N*-alkyl-carbazolylenes) linear decreasing dependencies result, the correlation factor being of  $R = 0.883$  and  $R = 0.970$ , respectively. For the poly(amides) the correlation factor is, however, of only  $R = 0.303$ . All other analyzed polymer classes show no somehow justifiable correlation between  $T_g/T_m$  and  $T_m$ .

Any attempt to prove correlations between glass and melting temperature of polymers has to consider the large uncertainty of data listed in literature, taking into account that the glass temperature is kinetically controlled (i.e., depends on cooling and heating rates), whereas the melting temperature depends on both crystallite size and shape as well on the overall crystallinity of the really semicrystalline polymers. Accordingly the scatter of reported data in literature will usually be large.

Nevertheless, in the following, an attempt is presented to evidence some peculiarities concerning the transition temperatures of polymers.

### Properties of polymer transition temperatures

In consideration of the fact that linear correlations between the glass temperatures and for mobility characteristic "mass/'flexible bonds' of monomeric (repeating) unit,"  $\mu/\rho$ , actually holds only within the different structural families of polymers, in Table I are listed the transition temperatures of seven arbitrarily chosen classes of polymers together with the most probable  $\mu/r$  values, taking into account of possible interactions. Except for poly(*N*-*n*-octyl-3,6-carbazolylene),<sup>17</sup> all listed data of glass temperatures,  $T_g$ ,<sup>18</sup> and melting temperatures,  $T_m$ ,<sup>19</sup> were extracted from the Polymer Handbook. Taking into account the lack of specifications concerning operational conditions and crystallinity, it is not surprisingly that in the literature are presented contradictory data for both  $T_g$  and  $T_m$ . Table I shows mean values together with the standard deviations of the contradictory data reported in literature.

Considering that the "flexibility" of polymers depends not only on the number of simple bonds of the monomeric unit, but also on both intra- and intermolecular interactions (hydrogen bonding for example), so the exact counting of the number of "flexible bonds" may be uncertain. Considering, for instance, that Figure 1 shows dependence of the polymer transition temperatures on the number of directly connected methylenes within the main or side chain spacers, it has been assumed that an increased probability

of development of crankshaft-like conformations between adjacent simple bonded  $\text{CH}_2$  units will promote crankshaft motions reducing the flexibility of the individual simple bonds. In addition were considered the possibilities of in plan or out-of-plan conformational position of stiff aromatic units, of steric hindrance among *ortho*-substituents or, between the oxygens of carboxylic groups as well as conformational nondiscernibility between identical substituents on main or side chain atoms.

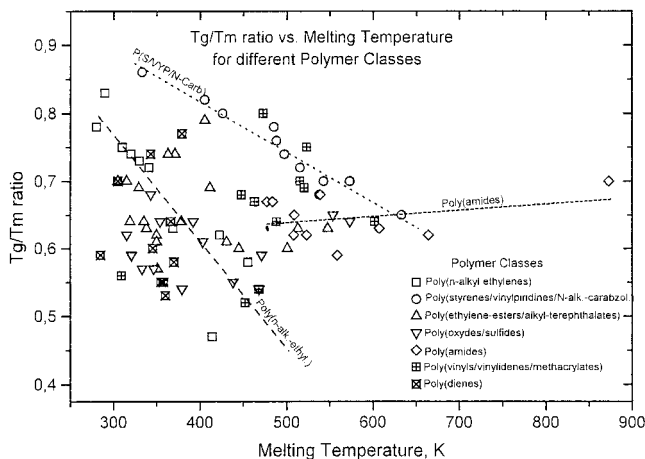
All this contributes to difficulties in an exact counting of the number of "flexible bonds" of the monomeric unit, additionally provoking an increasing scatter of data analyzed in terms of  $\mu/\rho$ .

Nevertheless, as shown in Figure 3, surprisingly not only the  $T_g$  vs.  $\mu/\rho$  correlations as emphasized before, but also the  $T_m$  vs.  $T_g$  dependencies hold, despite the large scatter of the data, in fact, rather well for the different structural classes of polymers.

Taking into account the same energetic background (cohesive energy density, CED) of the polymer transition temperatures and the overwhelming influence of conformational mobility, for the different polymer classes the dependence of the melting temperature on the mass/"flexible" bond of monomeric unit has subsequently been analyzed. The  $T_m$  vs.  $\mu/\rho$  correlations are analyzed comparative to the  $T_m$  vs.  $T_g$  and  $T_g$  vs.  $\mu/\rho$  dependencies. For clarity, the respective figures were split up.

Thus, for instance, in Figure 4(A) the  $T_m$  vs.  $T_g$  correlations are shown, whereas in Figure 4(B) the corresponding dependencies of the transition temperatures  $T_g$  and  $T_m$ , respectively, on  $\mu/\rho$  for poly(*n*-alkyl ethylenes), poly(styrenes)—including poly(vinylpyridine) and poly(*N*-*n*-alkyl-3,6-carbazolylenes) and poly(esters)—poly(ethylene-esters) and poly(*n*-alkyl-terephthalates), respectively. In Figure 5(A) and 5(B) the data of poly(oxydes/sulfides) and poly(amides) are exhibited, whereas in Figure 6(A) and (B) the respective data of poly(vinyls/vinylidenes) and poly(dienes) are shown.

Although the scatter of the data is relatively large, it unequivocally results that not only the  $T_g$  vs.  $\mu/\rho$  dependence is, as expected, polymer class specific, but also the respective  $T_m$  vs.  $T_g$  and the  $T_m$  vs.  $\mu/\rho$  correlations. It seems, however, that the sensibility is the higher for the melting temperature as it results in comparing, for instance, the respective correlations of  $T_m$  vs.  $\mu/\rho$  with  $T_g$  vs.  $\mu/\rho$  of poly(ethylene-esters) and poly(alkyl-terephthalates) [see Fig. 4(B)]. It may thus be assumed that the ordering induced by interaction has the greater influence on crystallization. This also explains the larger scatter of the  $T_m$  vs.  $T_g$  data of poly(vinyls/vinylidenes), taking into account the different tendency of hydrogen bond formation of the individual poly(vinyls/vinylidenes).



**Figure 2** Dependence of the  $T_g/T_m$  ratio on the melting temperature of different polymer classes according to eq. (4) of Matsuoka.<sup>16</sup>

The expressions of the belonging correlations obtained by linear fitting procedure according to the least-square method together with the respective correlations coefficients,  $R$ , are presented in Table II for the  $T_m$  vs.  $T_g$  dependencies and in Table III for the  $T_g$  vs.  $\mu/\rho$  and  $T_m$  vs.  $\mu/\rho$ , correlations, respectively.

**DISCUSSIONS**

Taking into account the experimentally (operational) conditioned scatter of both  $T_g$  and  $T_m$  data, the corre-

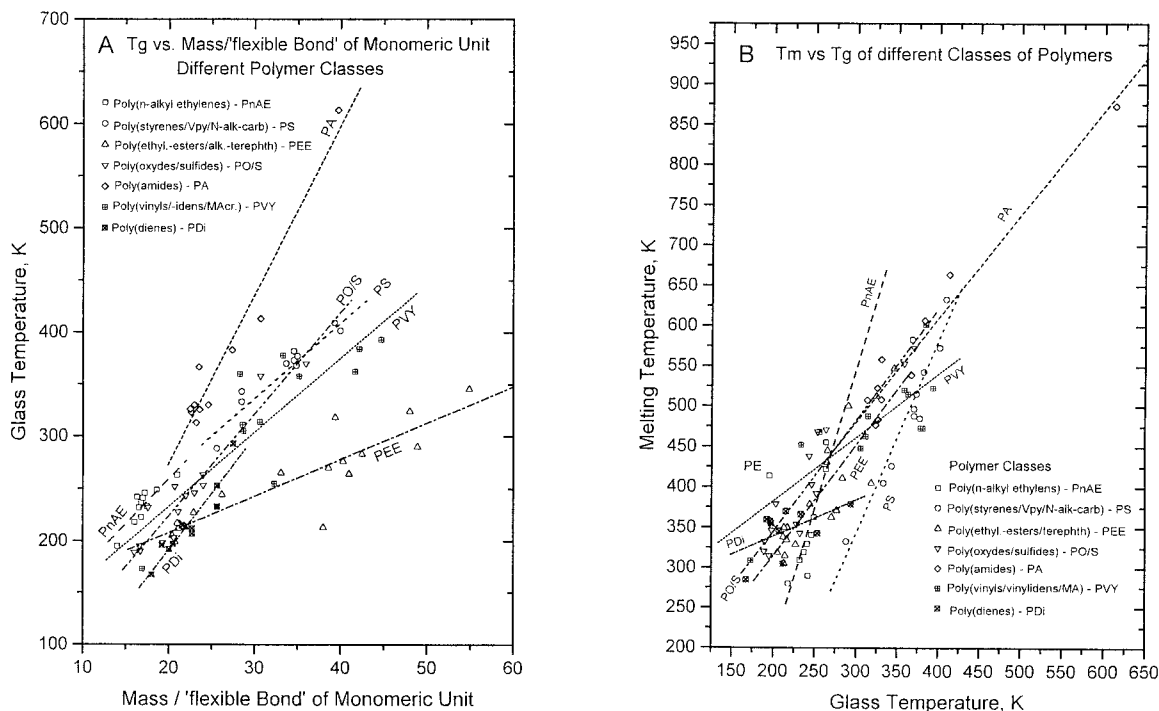
lation coefficients of the respective linear relations are, except the poly(dienes), in the usual range encountered for polymer characteristics. Surprisingly, the correlation coefficients of not only the glass temperature but also of the melting temperature dependencies on the mass/“flexible bonds” of monomeric unit are of the same quality.

In Table IV the slopes of the these correlations obtained by linear fitting procedure are compared.

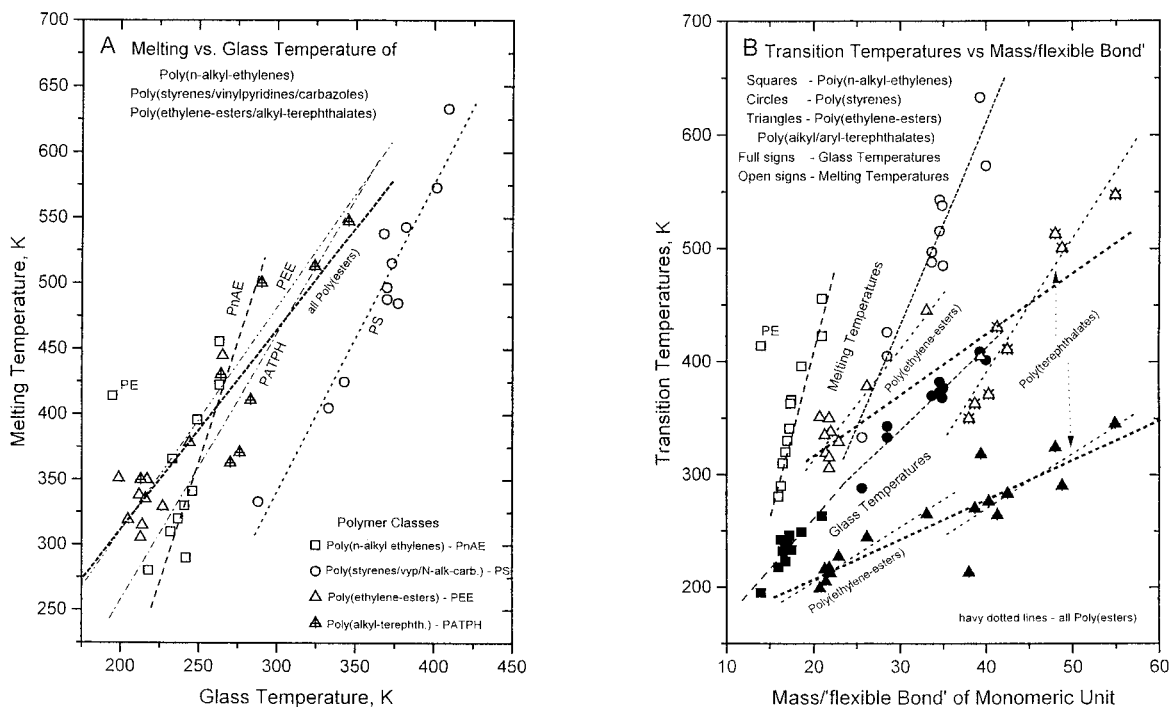
It unexpectedly resulted that the ratio between the slopes of the respective  $T_m$  vs.  $\mu/\rho$  and  $T_g$  vs.  $\mu/\rho$  dependencies are almost identical with the corresponding slopes of the  $T_m$  vs.  $T_g$  correlations. It may thus be supposed that the “flexibility” of the chemical bonds of the monomeric units controls not only the mobility of the polymers but also the belonging phase transitions.

Analyzing the magnitude of the of the slopes, they decrease in the succession poly(*n*-alkyl ethylenes) > poly(styrenes) [including poly(vinylpyridine) and poly(*N*-alkyl-carbazolylenes)] > poly(esters) [poly(ethylene-esters) and poly(alkyl-terephthalates)] > poly(oxydes/sulfides) > poly(amides) > poly(vinyls/vinylidens) > poly(dienes). It may thus be assumed that the mobility, and consequently, the “flexibility” of the simple bonds of the monomeric unit is additionally seriously affected by interactions.

For instance, the probability of interaction will, in fact, be almost negligible in saturated poly(*n*-alkyl ethylenes). Accordingly, the tendency of ordering, i.e.,



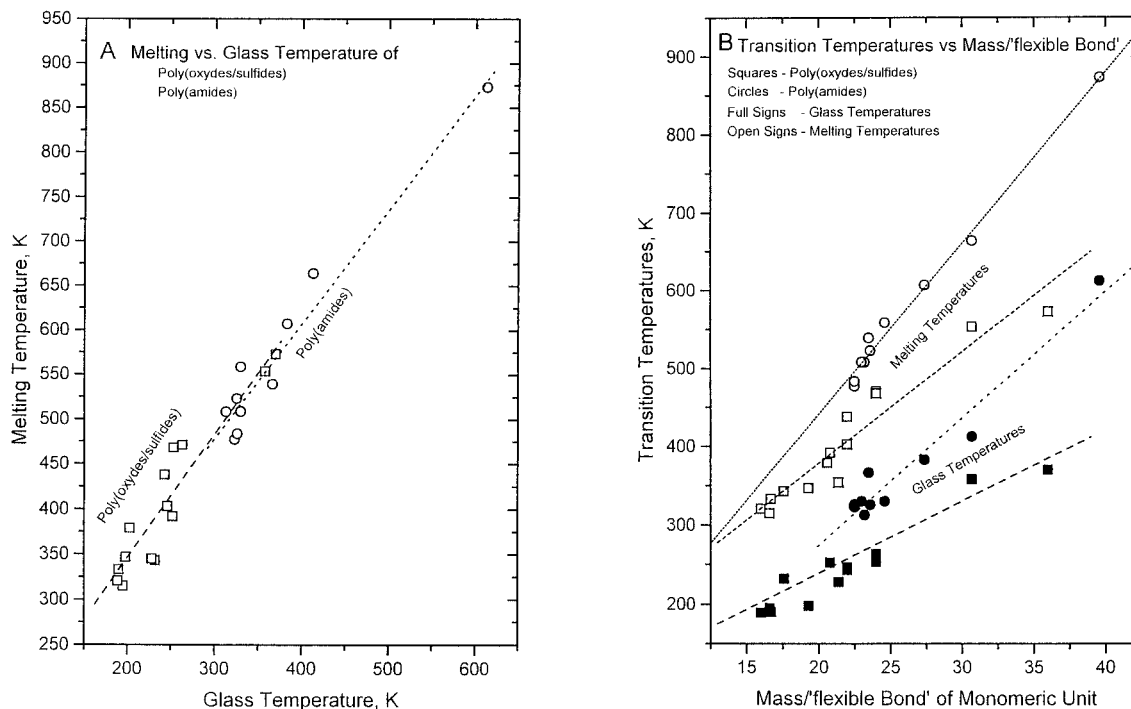
**Figure 3** Polymer class structure-specific behavior of transition temperatures. (A) The dependence of the glass temperature upon the “mass/‘flexible bond’ of monomeric unit” characteristics according to eq. (1) of Schneider and DiMarzio.<sup>7</sup> (B) Correlation between  $T_m$  and  $T_g$  of the different classes of polymers.



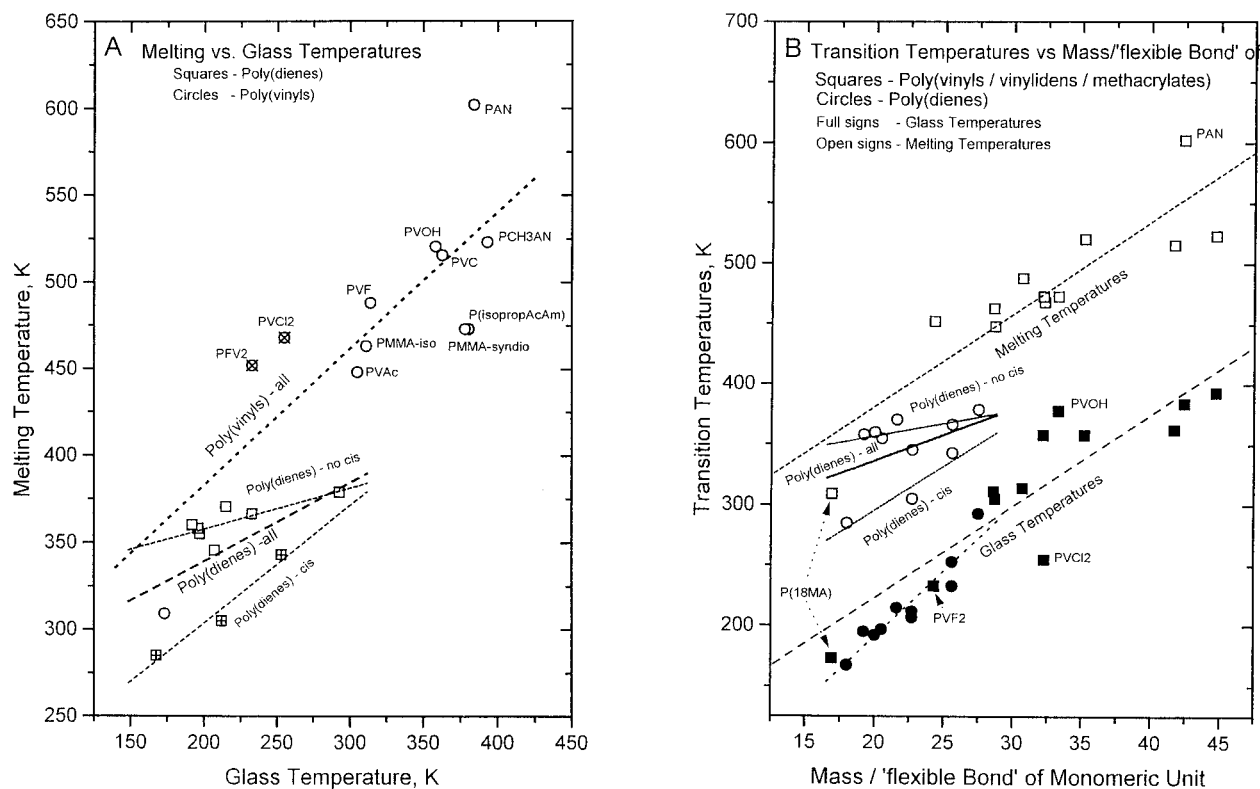
**Figure 4** Behavior of the transition temperatures of poly(*n*-alkyl ethylenes), poly(styrenes), and poly(estres). (A) Correlation between melting and glass temperature (B) Dependence of the transition temperatures upon the "mass/'flexible bond' of monomeric unit" characteristics.

the organization of the repeating units into a regular three-dimensional array showing the typical parallel alignment of portions of chain axes, will be small, which is the necessary condition of crystallization.

This tendency of ordering will additionally decrease with the size of the side chain of the saturated monomeric unit. Consequently, it may be assumed that the temperature difference between glass and crystalliza-



**Figure 5** Behavior of the transition temperatures of poly(oxydes/sulfides) and poly(amides). For (A) and (B), see Figure 4.



**Figure 6** Behavior of the transition temperatures of poly(vinyls/vinylidenes) and poly(dienes). For (A) and (B), see Figure 4.

tion temperature will increase considerably with increasing the size of the side chain, explaining the observed higher slope of the  $T_m$  vs.  $T_g$  correlation. In poly(dienes), on the contrary, interaction will be considerable promoted by the  $\pi$ - $\pi$  interacting double bonds distributed regular along the polymer main chain. Accordingly, the tendency of developing ordered structures will be substantially increased and less affected by the increasing size of the monomeric unit, which is confirmed by the observed reduced slope of the respective  $T_m$  vs.  $T_g$  correlation.

Considering the probability of interaction within the analyzed classes of polymers it may be supposed that the interaction increases with decreasing slope of the linear  $T_m$  vs.  $T_g$  correlation. Accordingly, the interaction will increase in the order of poly(*n*-alkyl ethylenes)—with almost no interaction < poly(sty-

renes/vinylpyridine/*N-n*-alkyl carbazolylenes)—possible  $\pi$ - $\pi$  interaction between the aromatic side chain rings < poly(ethylene-esters)/poly(alkyl-terephthalates)—interaction within and between the ester  $-C(=O)-O-$  groups < poly(oxydes/sulfides), including poly(aldehydes) < poly(amides) and poly(vinyls/vinylidenes)—possible increasing hydrogen bonding of both oxygen/sulfur and nitrogen as well as of the polar halogens. The interaction within poly(dienes) seems to be, accordingly, the chosen slope criterion the strongest.

It may thus be concluded that both the “flexibility” of polymers and the development of ordered structures promoting crystallization is decisively influenced by the probability of interaction between sequences of the polymer chain. Accordingly, the slope of the class-specific correlation between the melting

**TABLE II**  
Melting vs Glass Temperatures of Polymers Linear Correlations

Poly( <i>n</i> -alkyl ethylenes)	$T_m = -506.2 + 3.537 T_g$	$R = 0.847$
Poly(styrenes/vinylpyridines/ <i>N</i> -alkyl-3,5-carbazolylenes)	$T_m = -3.736 + 2.377 T_g$	$R = 0.960$
Poly(ethylene-esters/alkyl-terephthalates)	$T_m = 6.275 + 1.529 T_g$	$R = 0.907$
Poly(oxydes/sulfides)	$T_m = 66.174 + 1.388 T_g$	$R = 0.983$
Poly(amides)	$T_m = 94.172 + 1.289 T_g$	$R = 0.974$
Poly(vinyls/vinylidenes/methacrylates)	$T_m = 225.260 + 0.788 T_g$	$R = 0.805$
Poly(dienes) all	$T_m = 249.063 + 0.451 T_g$	$R = 0.544$
only <i>cis</i> -Poly(dienes)	$T_m = 168.663 + 0.675 T_g$	$R = 0.980$
Poly(dienes)—without <i>cis</i>	$T_m = 310.459 + 0.236 T_g$	$R = 0.763$



TABLE III  
Transition Temperatures vs. Mass/'flexible Bond' ( $\mu/\rho$ ) Linear Correlations

Glass temperatures $T_g$ vs. $\mu/\rho$		
Poly( <i>n</i> -alkyl ethylenes)	$T_g = 78.019 + 9.168 \mu/\rho$	$R = 0.878$
Poly(styrenes/vinylpyridines/ <i>N</i> -alkyl-3,5-carbazolylenes)	$T_g = 120.663 + 7.294 \mu/\rho$	$R = 0.960$
Poly(ethylene-esters/alkyl-terephthalates)	$T_g = 138.09 + 3.498 \mu/\rho$	$R = 0.898$
Poly(ethylene-esters)	$T_g = 105.395 + 4.970 \mu/\rho$	$R = 0.952$
Poly(alkyl-terephthalates)	$T_g = 72.912 + 4.918 \mu/\rho$	$R = 0.724$
Poly(oxydes/sulfides)	$T_g = 56.088 + 9.135 \mu/\rho$	$R = 0.774$
Poly(amides)	$T_g = -51.052 + 16.25 \mu/\rho$	$R = 0.973$
Poly(vinyls/vinylidens/MMA)	$T_g = 71.74 + 7.580 \mu/\rho$	$R = 0.875$
Poly(dienes) <sup>a</sup>	$T_g = -26.256 + 10.84 \mu/\rho$	$R = 0.944$
Melting temperatures $T_m$ vs. $\mu/\rho$		
Poly( <i>n</i> -alkyl ethylenes)	$T_m = -179.65 + 29.961 \mu/\rho$	$R = 0.952$
Poly(styrenes/vinylpyridines/ <i>N</i> -alkyl-3,5-carbazolylenes)	$T_m = -107.15 + 17.957 \mu/\rho$	$R = 0.955$
Poly(ethylene-esters/alkyl-terephthalates)	$T_m = 212.183 + 5.357 \mu/\rho$	$R = 0.896$
Poly(ethylene-esters)	$T_m = 119.434 + 9.745 \mu/\rho$	$R = 0.908$
Poly(terephthalates)	$T_m = -87.337 + 11.94 \mu/\rho$	$R = 0.908$
Poly(oxydes/sulfides)	$T_m = 90.873 + 14.36 \mu/\rho$	$R = 0.957$
Poly(amides)	$T_m = 21.689 + 21.96 \mu/\rho$	$R = 0.995$
Poly(vinyls/vinylidens/MMA)	$T_m = 227.919 + 7.673 \mu/\rho$	$R = 0.886$
Poly(dienes) all	$T_m = 250.389 + 4.313 \mu/\rho$	$R = 0.455$
Poly(dienes)— <i>cis</i>	$T_m = 149.494 + 7.308 \mu/\rho$	$R = 0.951$
Poly(dienes)—without <i>cis</i>	$T_m = 314.38 + 2.125 \mu/\rho$	$R = 0.595$

<sup>a</sup> All poly(dienes), including *cis*-derivatives exhibit the same  $T_g$  vs.  $\mu/\rho$  dependence.

temperature, characteristic of crystalline ordered structures and glass transition temperature, characteristic of the randomly distributed amorphous shares within semicrystalline polymers will be larger with the smaller probability of interaction promoting the development of ordered chain structures.

### CONCLUSION

The above-presented analysis of the correlations between the transition temperatures,  $T_g$  and  $T_m$ , of polymers, on the one hand, and their dependence on the "mass/'flexible bond' of monomeric unit" characteristics suggests that the mobility of the polymers is decisively influenced by the "flexibility" of simple

bonds. The ordering, promoting crystallization, seems to be additionally controlled by the probability of interaction between the sequences of the polymer chains. The notion of "flexible bonds" refers only to those simple bonds within the repeating unit, which, through energetically stimulated rotation, lead to conformation redistributions. Accordingly, not all simple bonds within the monomeric unit are at the same time "flexible bonds." Additionally, the "flexibility" of the simple bonds seems to be seriously influenced by interactions, thus explaining the class-specific behavior of polymers, taking into account the similar probabilities of interaction. It is consequently not surprising that the mobility of the polymers depends not only on the "flexibility" of the repeating units but also on

TABLE IV  
Slopes of the the Linear Correlations Melting vs. Glass Temperature of Polymers and  $T_m$  respective  $T_g$  vs. Mass "Flexible Bond" of Monomeric Unit

Polymer class	$T_m$ vs. $T_g$	$T_m$ vs. $\mu/\rho$	$T_g$ vs. $\mu/\rho$	$T_m$ vs. $\mu/\rho/T_g$ vs. $\mu/\rho$
Poly( <i>n</i> -alkyl ethylenes)	3.537	29.961	9.168	3.268
Poly(styrenes)	2.377	17.957	7.294	2.462
Poly(esters)—all	1.529	5.357	3.498	1.531
Poly(ethylene-esters)	1.819	9.745	4.970	1.961
Poly(alk.-terephthalates)	2.182	11.935	4.918	2.43
Poly(oxydes/sulfides)	1.388	14.356	9.135	1.572
Poly(amides)	1.289	21.964	16.245	1.35
Poly(vinyls/vinylidens)	0.788	7.672	7.580	1.012
Poly(dienes)—all	0.451	4.313	10.842 <sup>a</sup>	0.398
Poly(dienes)— <i>cis</i>	0.675	7.308	10.842	0.674
Poly(dienes) without <i>cis</i>	0.236	2.125	10.842	0.196

<sup>a</sup> All poly(dienes), including *cis*-derivatives exhibited the same  $T_g$  vs.  $\mu/\rho$  dependence.

the transition temperatures that are controlled by this polymer-specific characteristic. Taking into account the difficulties encountered in an exact counting of the number of "flexible bonds" of the monomeric unit and the class-specific dependence of this characteristics, it will generally be hard to correctly predict the transition temperatures of polymers without knowing the respective part of interactions.

This article is dedicated to Prof. Cantow's 80th anniversary with best wishes.

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