

Polymer class specificity of the glass temperature

Hans Adam Schneider*

Institut für Makromolekulare Chemie, 'Hermann-Staudinger-Haus', Freiburger Materialforschungszentrum, FMF, Stefan-Meier-Strasse 21, D-79104, Freiburg, Germany

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Abstract

It is shown that assuming linearity of the polymer class specific correlation between the glass transition temperature and the ratio mass to effective number of 'flexible' bonds of monomeric (repeat) unit, μ/ρ , it is possible to evaluate by least square fit the 'flexibility' factor, ρ , characterizing the share of those simple bonds within the repeat unit responsible for conformational rearrangements of the polymer. The evaluated effective number of simple bonds accounts for the influence of polymer class specific interactions and steric hindrances on the 'free rotation' of the simple bonds comprised in the repeat unit. It is shown that the well-known increase of the glass transition temperature of polymers bearing longer *n*-alkylic side chains may be the result of preferred 'crankshaft' like motions of neighboring methylenes, hindering the 'free rotation' of the simple bonds between the methylenes involved in the 'crankshaft'. It is also possible to quantify steric hindrances of bulky substituents.

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1. Introduction

The glass transition is a distinguishing mark of polymeric materials showing the characteristics of a second-order thermodynamic transition (e.g. continuity of volume, enthalpy and other first order derivatives of the Gibbs free energy, but discontinuity of the second order derivatives, i.e. expansion coefficient, heat capacity, etc.) [1]. However, the experimentally observed frequency and time dependence points to the fact that the transition does not occur under thermodynamic equilibrium condition, the polymer being 'frozen-in'. Accordingly polymeric glasses show relaxation phenomena which depend on 'relaxation entropy' and 'free volume', being controlled by the tendency of the 'metastable' glass to approach thermodynamic equilibrium ('aging' of polymers). Thus two main models have been developed for the theoretical description of the glass transition phenomenon: the kinetic based 'free volume' and the thermodynamic based 'conformational entropy' theory.

The kinetic theory assumes that the mobility of molecules is controlled by the 'free volume' and the glass transition occurs as soon as the temperature dependent decrease of the free volume within the amorphous phase reaches some characteristic value preventing any further molecular rearrangements [2].

According to the thermodynamic theory the glass is considered a fourth state of matter, characterized by 'zero-conformational' entropy which can be evaluated in terms of an 'S-V-T' equation of state [3]. The transition to the thermodynamic stable glass is characterized in this state diagram by a second-order transition temperature, T_2 , situated about 50 K below the experimentally observable glass temperature, T_g . Conformational changes contributing to the conformational entropy are controlled by 'flexible bonds', i.e. those simple bonds which by rotation allow conformational changes of the molecule.

Unfortunately there is no way to verify experimentally the validity of any of these two theories. Because of the kinetic dependent 'freeze-in' phenomenon of the glass transition, the calculated second-order transition, T_2 , is experimentally not accessible, whereas the estimated values

* Fax: +49-761-203-4730.

E-mail address: hanserna@t-online.de.

of ‘free volume’ differ, depending on the definition used, by several orders of magnitude [4].

Besides the molecular weight (through ‘chain end effects’) and the degree of crosslinking [5] the glass transition temperature of polymers depends on a series of molecular parameters, the prevailing two factors being the chain flexibility related to the characteristic ratio [6] and the inter/intramolecular interactions characterized by the cohesive energy density [7].

The chain flexibility is first of all controlled by the barrier to rotation of the backbone C–C bonds. The larger the substituent and the stronger the interaction between substituents the more hindered will be this rotation. Additionally the hindrance to rotation is accentuated by multiple anchoring on the same C (two or three substituents) increasing the glass transition temperature.

On the other hand longer *n*-alkylic side chains lower the glass transition temperature due to an internal ‘plasticizing effect’ of the main chain. Natta et al. [8] have shown already in 1957 the plasticizing effect of short *n*-alkylic side chains on the glass transition temperature of poly(α -olefin)s.

Taking into account both the theoretical and technological importance of knowing the glass transition of polymers, several semiempirical methods have been suggested in literature for predicting T_g . One of these methods scales the volume contributions to T_g of the different chemical constituents of the repeating unit [9]. Hopfinger et al. [10] have developed a model to estimate T_g using conformational flexibility and mass moments, assuming group additivity and correlating by least square fit the calculated values with experimental T_g -data. The model has subsequently been extended to account for intermolecular contributions [11].

Schneider and DiMarzio [12] suggested the more simple correlation of T_g with the mass per ‘flexible’ bond of the monomeric (repeat) unit

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

with μ the mass and ρ the number of ‘flexible’ bonds of the monomeric unit. A and C are polymer class specific constants being associated with the very similar interactions and hindrances within a given class of polymers [13]. The prevailing problem of this correlation is related to the exact counting of the effective number of ‘flexible’ bonds contributing by rotation to conformational changes of the repeat unit because of unknown hindrances due to inter/intramolecular interactions and steric effects. Nevertheless the scatter of the data is not larger than for the other proposed semiempirical correlations [13,14].

2. Dependence of the glass temperature on the length of *n*-alkylic side chain and the bulkiness of substituents

In order to show the influence of the length of *n*-alkylic side chains and of the bulkiness of substituents

on the glass transition temperature of polymers, T_g , data were taken from the ‘Polymer Handbook’ [15] for five classes of polymers. They are presented in Table 1. Taking into account the very conflicting data in the literature for poly(ethylene) the value of Boyer [16] has been used in the following discussion.

2.1. Influence of the bulkiness of the side-group of mono-substituted polymers

It is known that the glass transition temperature of mono-substituted polymers increases with the bulkiness of the substituent. It is, however, surprising that the increase of the glass transition temperature of poly(α -olefin)s seems to be directly proportional to the atomic mass of the substituents. For the other classes of polymers studied this general tendency of T_g -increase to the atomic mass of the substituent is confirmed, but the scatter of the data is, however, much larger (see signs with question-marks in Fig. 1).

For instance, the glass transition temperatures of all other *iso*-propyl substituted polymers are much smaller than expected from the atomic mass of the substituent. The observed higher T_g -values of the poly(phenyl acrylic/methacrylic ester)s compared to those of the heavier poly(cyclohexyl ester)s may be explained by additional hindrances of the free rotation of the

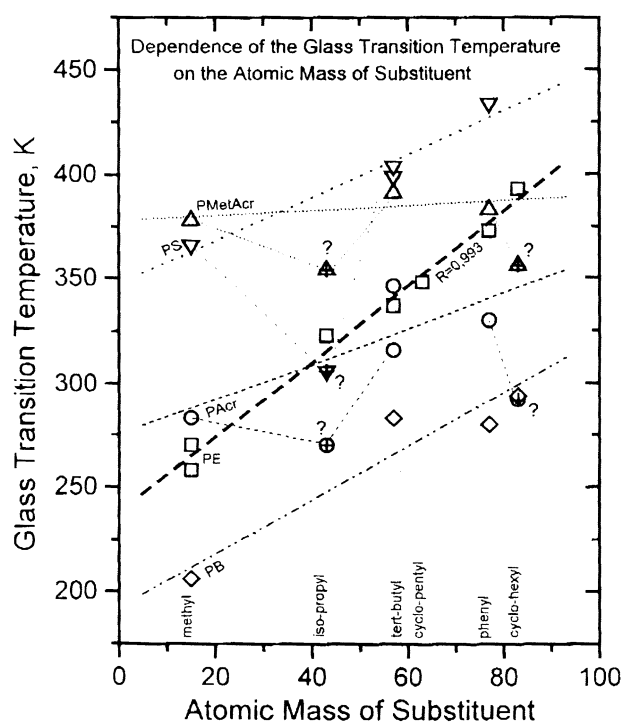


Fig. 1. Dependence of the glass transition temperature on the atomic mass of substituents. PE, poly(ethylene)s; PS, poly(styrene)s; PMetAcr, poly(methacrylic ester)s; PAcr, poly(acrylic ester)s; PB, poly(butadiene)s lines by linear fit (symbols with crosses being neglected).

Table 1
Glass temperatures of polymers bearing *n*-alkylic side chains or alkylic/arylic substituents

Polymer	x^a	T_g (K) ^b	μ/ρ^c	
			Simple ^d	Crankshaft ^e
Poly(olefin)s				
Poly(ethylene)	148	220–240 ^f	28/2	195 (± 10) ^g
Poly(<i>n</i> -alkyl ethylene)s				
Poly(methyl-ethylene)=Poly(propylene), atactic	0	258–270	42/2	
Poly(ethyl-ethylene)	1	249	56/3	
Poly(<i>n</i> -propyl-ethylene)	2	233	70/4	
Poly(<i>n</i> -butyl-ethylene)	3	223	84/5	
Poly(<i>n</i> -pentyl-ethylene)	4	242	98/6	98/5.5
Poly(<i>n</i> -hexyl-ethylene)	5	208, 228	112/7	112/6.5
Poly(<i>n</i> -heptyl-ethylene)	6	226	126/8	126/7.5
Poly(<i>n</i> -octyl-ethylene)	7	232	140/9	140/8
Poly(<i>n</i> -nonyl-ethylene)	8	236	154/10	154/8.5
Poly(<i>n</i> -decyl-ethylene)	9	237	168/11	168/9.5
Poly(<i>n</i> -dodecyl-ethylene)	11	241	196/13	196/10.5
Poly(<i>n</i> -tetradecyl-ethylene)	13	246	224/15	224/11.5
Poly(alkyl/aryl ethylene)s				
Poly(<i>iso</i> -propyl-ethylene)		323		70/3 ^h
Poly(<i>iso</i> -butyl-ethylene)		302		84/3.5 ^h
Poly(<i>tert</i> -butyl-ethylene)		337		84/3 ^h
Poly(cyclohexyl-ethylene), atactic		393		110/3.5 ⁱ
Poly(phenyl-ethylene)=Poly(styrene)		373		104/3.5 ^j
Poly(acrylate/methacrylate)s				
Poly(acrylic acid)		379		72/2.5 ^k
Poly(<i>n</i> -alkyl acrylic ester)s				
Poly(methyl acrylate)	0	283	86/3.5 ^l	
Poly(ethyl acrylate)	1	249	100/4.5	
Poly(propyl acrylate)	2	236	114/5.5	
Poly(butyl acrylate)	3	219	128/6.5	
Poly(hexyl acrylate)	5	216	156/8.5	156/8
Poly(heptyl acrylate)	6	213	170/9.5	170/9
Poly(octyl acrylate)	7	208	184/10.5	184/9.5
Poly(nonyl acrylate)	8	215	198/11.5	198/10
Poly(dodecyl acrylate)	11	270	240/14.5	240/10.5
Poly(tetradecyl acrylate)	13	297	268/16.5	268/11
Poly(hexadecyl acrylate)	15	308	296/18.5	296/11.5
Poly(alkyl/aryl acrylic ester)s				
Poly(<i>iso</i> -propyl acrylate)		267–270		114/5 ^h
Poly(<i>iso</i> -butyl acrylate)		249		128/6 ^h
Poly(<i>tert</i> -butyl acrylate)		316–346		128/4.5 ^h
Poly(cyclohexyl acrylate)		292		154/6 ⁱ
Poly(phenyl acrylate)		330		148/5.5 ^j
Poly(methacrylic acid)		501		86/2.5 ^k
Poly(<i>n</i> -alkyl methacrylic ester)s				
Poly(methyl methacrylate)	0	378	100/3.5 ^l	
Poly(ethyl methacrylate)	1	333	114/4.5	
Poly(propyl methacrylate)	2	308	128/5.5	
Poly(butyl methacrylate)	3	293	142/6.5	
Poly(pentyl methacrylate)	4	268	156/7.5	
Poly(hexyl methacrylate)	5	268	170/8.5	170/8
Poly(octyl methacrylate)	7	228	198/10.5	198/9.5
Poly(decyl methacrylate)	9	203	226/12.5	226/11
Poly(dodecyl methacrylate)	11	208	254/14.5	254/12.5
Poly(tetradecyl methacrylate)	13	232	282/16.5	282/13
Poly(alkyl/aryl methacrylic ester)s				
Poly(<i>iso</i> -propyl methacrylate)		354		128/4.5 ^h
Poly(<i>iso</i> -butyl methacrylate)		326		142/5.5 ^h
Poly(<i>tert</i> -butyl methacrylate)		391		142/4.5 ^h
Poly(cyclohexyl methacrylate)		356		168/6 ⁱ
Poly(phenyl methacrylate)		381		162/5.5 ^j

Table 1 (continued)

Polymer	x^a	T_g (K) ^b	μ/ρ^c	
			Simple ^d	Crankshaft ^e
Poly(styrene)		373–377		104/3.5 ^k
Poly(4- <i>n</i> -alkyl styrene)s				
Poly(4-methyl-styrene)	0	371–375	118/4	
Poly(4-ethyl-styrene)	1	300, <350	132/5	
Poly(4-butyl-styrene)	3	279	160/7	
Poly(4-hexyl-styrene)	5	246	188/9	188/8.5
Poly(4-octyl-styrene)	7	228	216/11	216/10
Poly(4-nonyl-styrene)	8	220	230/12	230/11
Poly(4-decyl-styrene)	9	208	244/13	244/12
Poly(4-dodecyl-styrene)	11	221	272/15	272/12.5
Poly(4-tetradecyl-styrene)	13	237	300/17	300/13.5
Poly(4-hexadecyl-styrene)	15	279	328/19	328/14
Poly(4-octadecyl-styrene)	17	305	356/21	356/14.5
Poly(4-nonadecyl-styrene)	18	305	370/22	370/15
Poly(4-alkyl/aryl styrene)s				
Poly(4-isopropyl-styrene)		306		146/5.5 ^h
Poly(4- <i>sec</i> -butyl-styrene)		359		160/5.5 ^h
Poly(4- <i>tert</i> -butyl-styrene)		399, 404		160/5 ^h
Poly(4-phenyl-styrene)		429		180/5.5 ^j
Poly(butadiene)s				
Poly(butadiene), Poly(1-butylene)				
<i>Cis</i>		164–171		54/4 ^m
<i>Trans</i>		215		54/3
Poly(1- <i>n</i> -alkyl-1-butylenes)				
Poly(isoprene), Poly(2-methyl-1-butylene)				
<i>Cis</i>	0	200, 206–218	68/4.5	
<i>Trans</i>		207–215	68/4.5	
Poly(1-ethyl-1-butylene)	1	197	82/5	
Poly(1-propyl-1-butylene)	2	196	96/6	
Poly(1-butyl-1-butylene)	3	192	110/7	
Poly(1-heptyl-1-butylene)	6	190	152/10	152/9.5
Poly(1-decyl-1-butylene)	9	220	194/13	194/10.5
Poly(1-alkyl/aryl-1butylene)s				
Poly(1- <i>iso</i> -propyl-1-butylene)		221		96/5 ^h
Poly(1- <i>tert</i> -butyl-1-butylene)		293		110/4.5 ^h
Poly(1-phenyl-1-butylene)		283		130/5 ^j

^a Number of methylenes between main chain and end-methyl group of the *n*-alkylic side chain.

^b T_g -data taken from Peysner [15].

^c Mass/‘flexible’ bond of repeat (monomeric) unit.

^d All simple bonds, except of the bond of side chain end-methyl group are counted to be ‘flexible’ bonds.

^e Possible ‘crankshaft’ movements of at least 4 neighboring methylenes will hinder the free rotation of the simple bonds between the methylenes involved in the ‘crankshaft’.

^f Conflicting interpretation of PE T_g data, see [15].

^g T_g -data of Boyer [16].

^h Multiple anchoring of methyls to the same C-atom will hinder their free rotation.

ⁱ For cyclohexane are considered the two possible conformations.

^j The stiff phenyl ring may be arranged in or out of the main-chain plane, additionally it may be stiffened in esters by π – π interaction with the free electrons of the oxygen of the acidic group, or with the adjacent phenyl of PS and the double bonds of polydiene, respectively.

^k Possible hydrogen bonding reduces the ‘flexibility’ of the free acidic group.

^l Substitution of the acidic hydrogen will liberate the flexibility of –COO– in polyesters.

^m Favoured ‘crankshaft’ motion of the backbone of the repeat units increases the ‘flexibility’ of *cis*-butadiene compared to *trans*-butadiene, where ‘crankshaft’ arrangements of the repeat units are structurally less probable.

phenyl-ring caused by π – π interactions of the phenyl with the free electrons of the oxygen of the acidic –COO– group, and in poly(4-phenyl-styrene) by the π – π interaction with the neighboring phenyl of polystyrene, respectively.

2.2. Influence of the length of the *n*-alkylic side chain on T_g

As mentioned before, the experimentally observed decrease of the glass transition temperature of poly(α -olefin)s with the length of the *n*-alkylic side chain has been

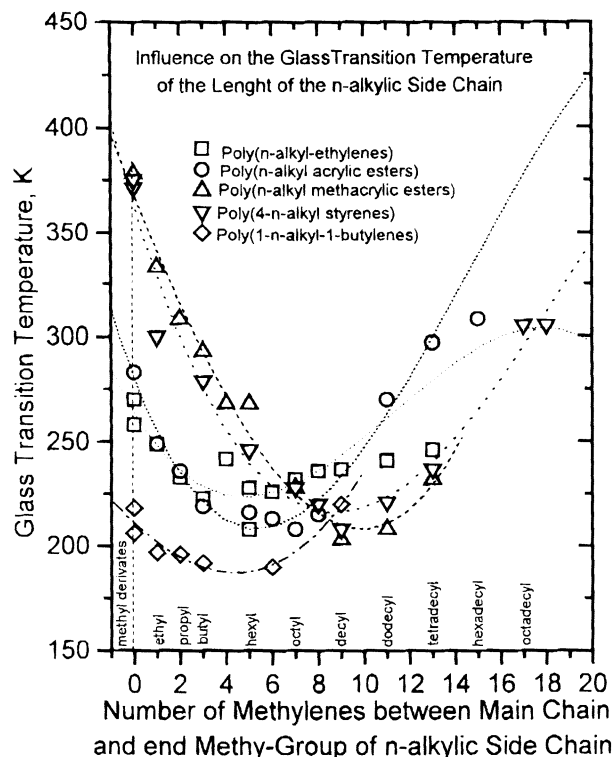


Fig. 2. Dependence of the glass transition temperature on the length of the *n*-alkylic side chain bearing methyl end-groups; lines by third order fit.

attributed to an internal ‘plasticizing effect’ [8]. The data exhibited in Fig. 2 show that this ‘plasticizing effect’ is general for all classes of polymers studied, but the T_g lowering effect ends for polymers with the longer *n*-alkylic side chains. T_g increases anew for the polymers bearing longer *n*-alkylic side chains. The glass transition temperatures show a minimum at the *n*-hexyl/*n*-octyl derivatives of the more flexible main chains [i.e. poly(α -olefin)s, poly(*n*-alkyl acrylate)s and poly(*n*-alkyl butadiene)s] and at *n*-octyl/*n*-decyl for the derivatives of the stiffer poly(*n*-alkyl methacrylate)s and poly(4-*n*-alkyl styrene)s, respectively.

Side chain crystallization is the explanation usually invoked in the literature to account for the observed increase of T_g of the higher *n*-alkylic side chain polymers. According to this assumption, side chain crystallization leads to a denser packing of the polymer accompanied by a corresponding decrease of the ‘free volume’ and thus by an increase of T_g .

A second possible explanation which will be presented in the following starts with the supposition that possible ‘crankshaft’ like motions of at least 4 adjacent methylenes within the *n*-alkylic side chain reduces the effective ‘flexibility’ of $-\text{CH}_2-\text{CH}_2-$ simple bonds involved in the ‘crankshaft’, reducing thus the overall ‘flexibility’ of the repeat unit. This assumption is supported by the T_g data shown for the poly(*n*-alkyl ethylene)s in Fig. 3(A).

This ‘crankshaft’ like motions of groups of 4 neighboring methylenes will hinder the ‘free rotation’ of the within involved individual $-\text{CH}_2-\text{CH}_2-$ simple bonds reducing

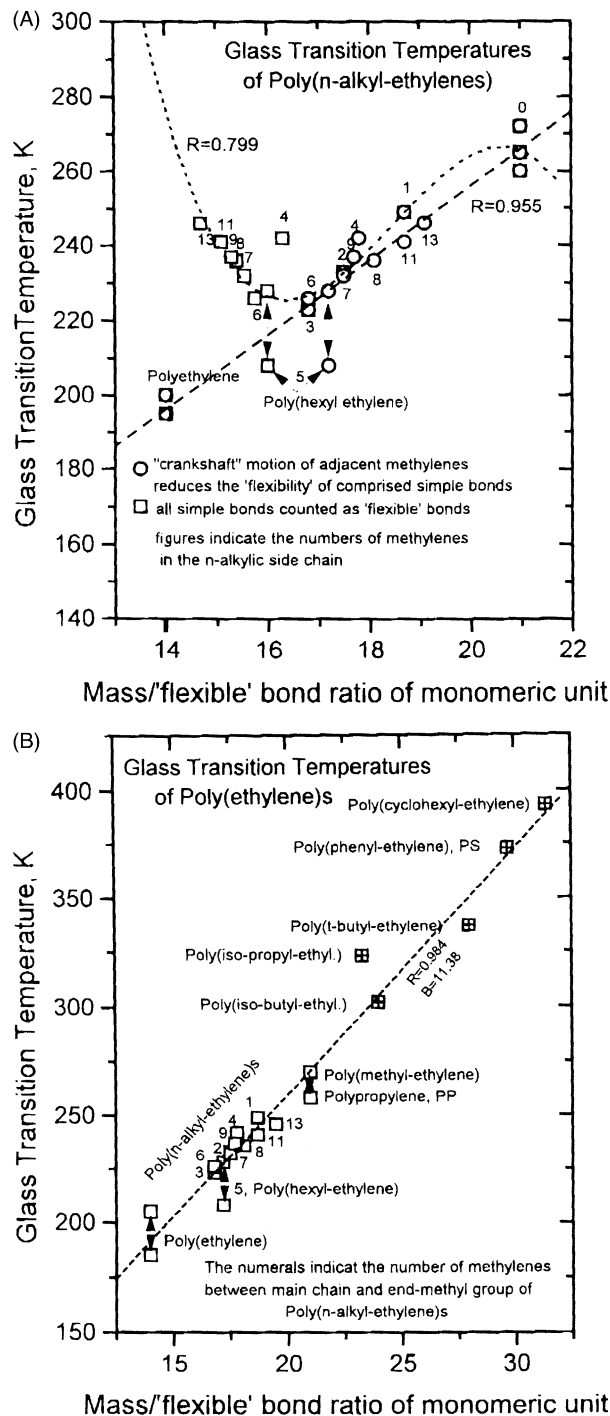


Fig. 3. (A) Dependence of the glass transition temperature of poly(*n*-alkyl ethylene)s on the mass/‘flexible’ bond ratio of monomeric unit open squares—all simple bonds are counted as ‘flexible’ bonds contributing by ‘free rotation’ to conformational rearrangements; line by third order fit open circles—hindering effect of ‘crankshaft’ like motions of at least four neighboring methylenes on the ‘free rotation’ of the methylenes of the ‘crankshaft’; line by linear fit. (B) Dependence of the glass transition temperature of poly(ethylene)s on the ‘flexibility’ (mass/‘flexible’ bonds ratio) of the monomeric unit accounting for hindrances by ‘crankshaft’ like motions and steric effects of bulky alkylic/arylic substituents, respectively open signs: *n*-alkylic side-chain derivatives; signs with crosses: bulky alkylic/arylic substituents; line by linear fit.

consequently the effective number of ‘flexible’ bonds compared to the overall number of simple bonds of the n -alkylic side chain as shown in Table 1. (Compare columns ‘simple’ and ‘crankshaft’ of the heading μ/ρ). In accordance with the Schneider–DiMarzio rule (Eq. (1)), the result of this assumption is supported by the linearity of the corresponding T_g vs. μ/ρ data (shown by circles). Counting, on the contrary, all simple bonds within the n -alkylic side chain as ‘flexible’ bonds the respective data (squares) show a minimum. Unfortunately, the determination of the exact number of ‘flexible’ bonds, assuming hindrances by ‘crankshaft’ motions is only possible by a least squares fit to a straight line of the T_g vs. μ/ρ correlation. It is interesting to note that extrapolation of the resulting linear T_g vs. μ/ρ correlation of poly(n -alkyl ethylene)s confirms the T_g value of Boyer [16] for ‘amorphous’ poly(ethylene) deduced by extrapolation of poly(ethylene) T_g -data for zero crystallinity.

In Fig. 3(B) are shown the glass transition temperatures of all poly(olefin)s listed in Table 1, as well as those of poly(alkyl/aryl ethylene)s (symbolized by crosses) to evidence in addition the effect of the bulkiness of the different substituents on the overall ‘flexibility’ of the respective monomeric units. It is worth mentioning that the linearity correlation factor of $R=0.984$ is astonishingly good. B is the slope of the linear T_g vs. μ/ρ correlation.

Using the same procedure we obtained similarly satisfactory linear T_g vs. μ/ρ correlations for all other polymers listed in Table 1 bearing n -alkylic side chains and alkyl/arylic bulky substituents, respectively. The resulting correlation factors, R , and the slopes of the obtained straight lines, B , are shown in the respective plots; in Fig. 4(A) for poly(acrylic/methacrylic ester)s and in Fig. 4(B) for poly(4-alkyl/aryl styrene)s and poly(1-alkyl/aryl-1-butylene)s, i.e. poly(diene)s.

The correlation factors, R , and the belonging slopes, B , of the T_g vs. μ/ρ straight lines of the analyzed polymer classes bearing n -alkylic side chains (including derivatives with bulky alkyl/arylic substituents) are listed in Table 2. It is interesting to mention that the values of the correlation factors are surprisingly good taking into account the fit method used to evaluate the effective number of ‘flexible’ bonds of the n -alkylic side chain derivatives. The different slopes of the T_g vs. μ/ρ correlations of the studied polymer classes support the assumption that similar interactions and hindrances are acting within a given class of polymers.

It is, however, unexpected that the slopes of the T_g vs. μ/ρ linear correlations increase with the decrease of the ‘flexibility’ of the repeat units. This is reflected in the generally higher T_g -values of the same derivatives of the studied polymers. In Table 2 are listed for comparison the T_g values of the respective methyl derivatives.

Finally in Fig. 5(A) are shown the ‘flexibility’ factors, ρ , deduced by the least square fit procedure used to draw the respective T_g vs. μ/ρ linear correlations of the different classes of polymers bearing n -alkylic side chains. For better

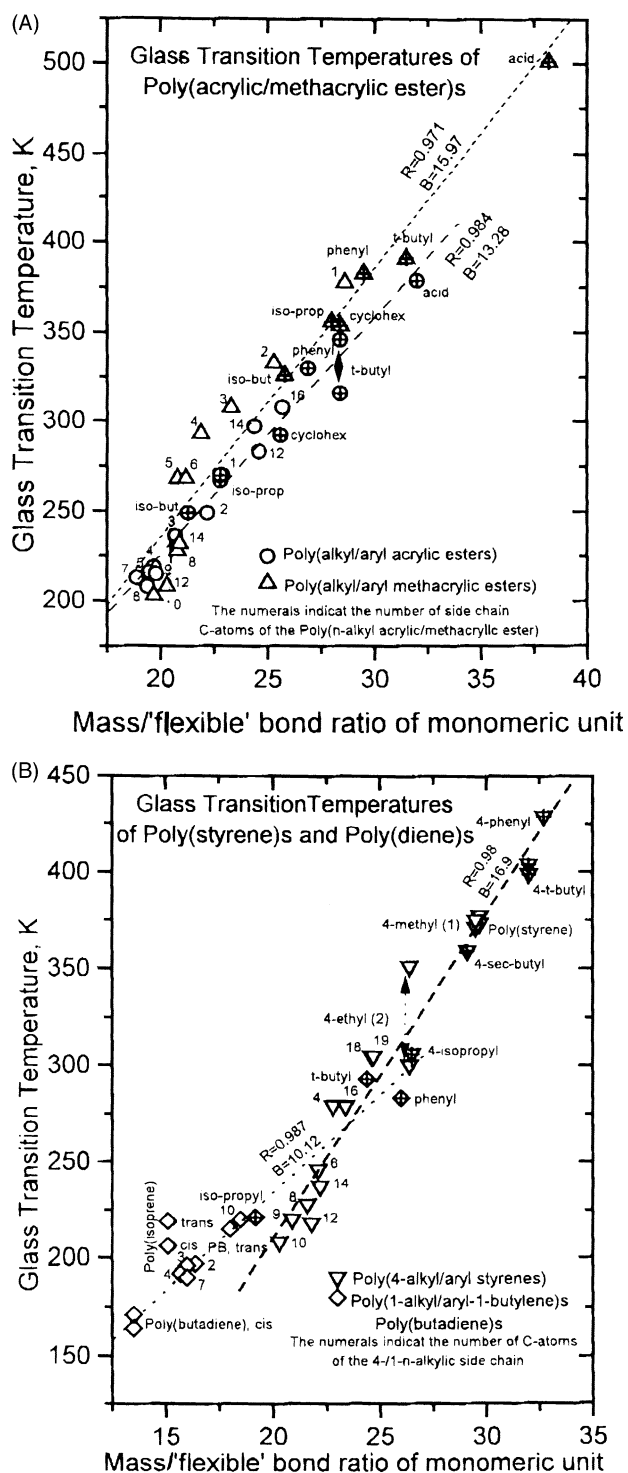


Fig. 4. (A) Dependence of the glass transition temperature of poly(acrylic-) and poly(methacrylic ester)s on the ‘flexibility’ of the monomeric unit accounting for possible ‘crankshaft’ like and steric hindrances. For significance of open and crossed symbols, see Fig. 3(B); lines by linear fit. (B) Dependence of the glass transition temperature of poly(styrene)s and poly(butadiene)s on the ‘flexibility’ of the monomeric unit accounting for possible ‘crankshaft’ like and steric hindrances. For significance of open and crossed signs, see Fig. 3(B); lines by linear fit.

Table 2
Correlation factors and slopes of the T_g vs. μ/ρ straight lines

Polymer class	R corr.f	B slope	T_g , K of methyl derivatives
Poly(1- <i>n</i> -alkyl-1-butylene)s	0.987	10.12	206–218
Poly(<i>n</i> -alkyl-ethylene)s	0.984	11.38	258–270
Poly(<i>n</i> -alkyl-acrylic ester)s	0.984	13.28	283
Poly(<i>n</i> -alkyl-methacrylic ester)s	0.971	15.97	378
Poly(4- <i>n</i> -alkyl styrene)s	0.980	16.90	375

comparison in Fig. 5(B) are presented normalized ‘flexibility’ factors evaluated as differences between the ‘flexibility’ factors of the various *n*-alkylic side chain derivatives and the respective methyl derivative. Except for the higher *n*-alkyl derivatives of the poly(*n*-alkyl acrylic ester)s the agreement between the ‘normalized’ flexibility factors of the different classes of polymers is amazingly good. This is confirmed by the correlation factor of $R=0.998$ of the accepted third order fitting equation. This proves that the hindering effect of crankshaft motions of at least four neighboring side chain methylenes on the ‘free rotation’ of simple bonds between the methylenes included in the crankshaft is the same, irrespective of the nature of the polymeric backbone.

It is interesting to notice that cooperative trans–gauche ‘crankshaft’ like motions in poly(ethylene) have been involved to explain the experimentally observed different characteristic ‘freeze-in’ processes of poly(ethylene) showing distinct T_g values [17,18].

The same procedure to evaluate ‘normalized’ flexibility factors was used for derivatives bearing bulky substituents. This showed that the diverse classes of polymers studied have different linear correlations suggesting specific interactions between the polymeric backbone and the bulky substituents. (see Fig. 6). So, for instance, the derivatives with bulky substituents of poly(acrylic-) and poly(methacrylic ester)s show the same ‘normalized’ flexibility factors, differing from those of the derivatives of poly(ethylene)/poly(styrene) and poly(butadiene), respectively.

3. Conclusions

Least square fits were used to evaluate ‘flexibility’ factors, ρ , from the linear correlation between the glass transition temperature and the mass/‘flexible’ bond ratio of the monomeric unit (T_g vs. μ/ρ). The ‘flexibility’ factors account for polymer class specific interactions and steric hindrances on the ‘free’ rotation of those simple bonds responsible for conformational rearrangements. Applying

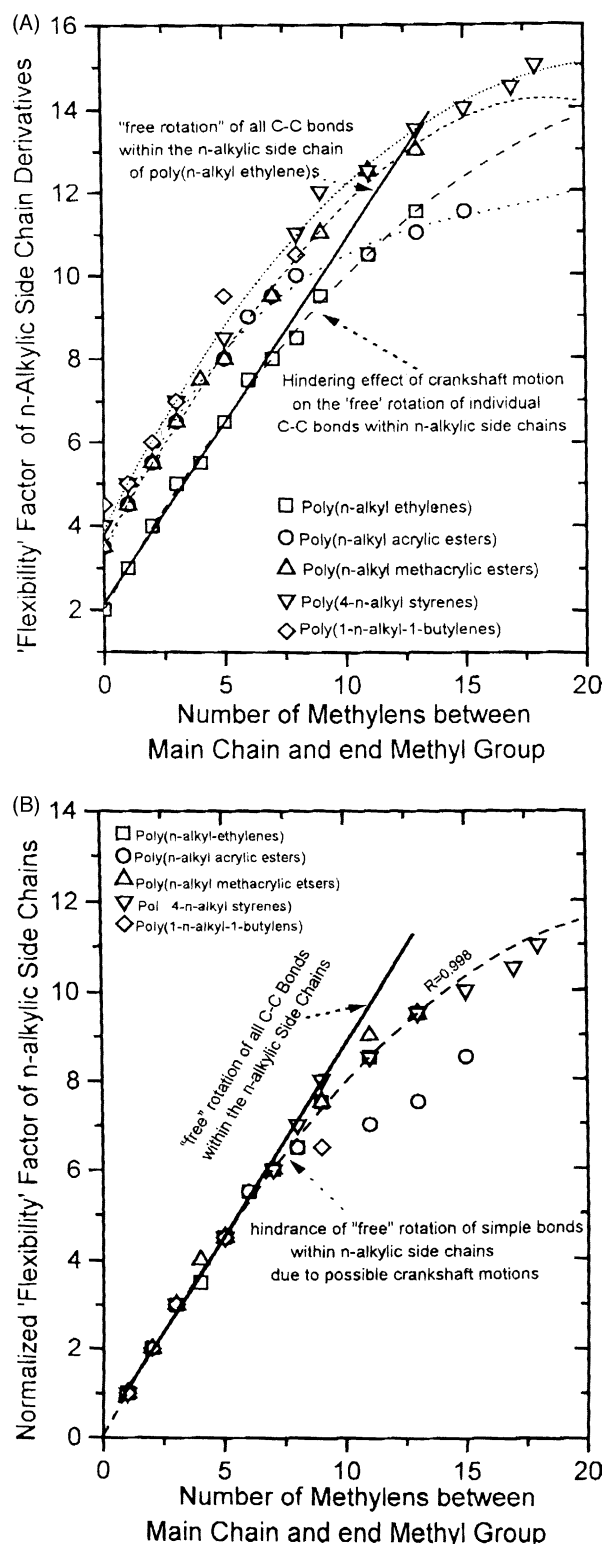


Fig. 5. (A) Dependence of the ‘flexibility’ factor of *n*-alkylic side chains derivatives on the number of methylenes to the methyl end-group evidencing the hindering effect of ‘crankshaft’ like motions on the ‘free rotation’ of simple bonds; lines by third order fit. (B) Dependence of the normalized ‘flexibility’ factor of *n*-alkylic side chains on the number of methylenes to the methyl end-group; line by third order fit.

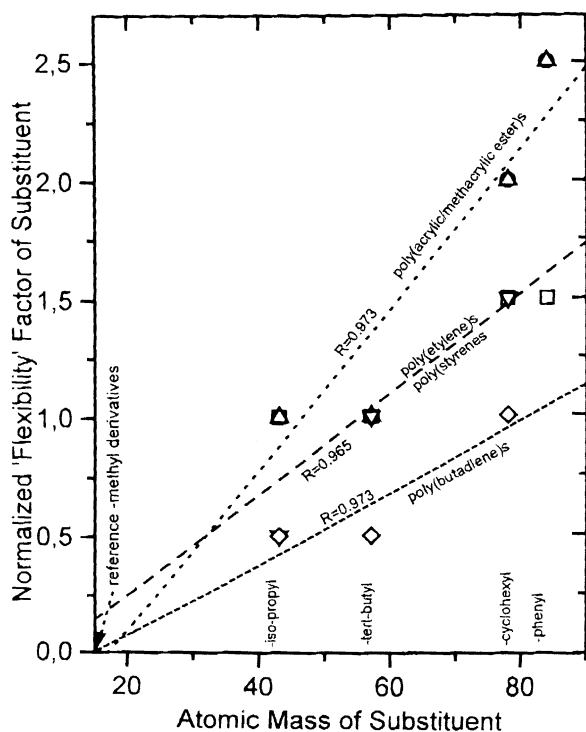


Fig. 6. Dependence of the normalized 'flexibility' factor on the atomic mass of bulky substituents connected directly to the basic monomeric unit. For significance of the symbols see Fig. 5(B).

this procedure it is shown that the experimentally observed renewed increase of the glass transition temperature of polymers bearing longer *n*-alkylic side chains may be explained not only by the typically assumed, but in our opinion less probable side chain crystallization, but also by supposing 'crankshaft' like motions of at least four neighboring methylenes which will hinder the 'free' rotation of the simple bonds between the methylenes involved in the 'crankshaft' structure.

We would also like to point out that the normalized 'flexibility' factors deduced by fits and expressed by the difference between the respective 'flexibility' factors, of the

longer *n*-alkylic side chains and the corresponding methylic derivatives are the same for the different classes of polymers studied, although generally the T_g vs. μ/ρ behavior is polymer specific. However, the polymer class specificity is reflected by both the overall T_g vs. μ/ρ behavior of the analyzed polymer classes as well by the normalized 'flexibility' factors of the different bulky substituents.

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