Influence of a functional group situated along the n-alkyl side chain on the γ-transition of comb-like polymers: Poly[*N*-(5-n-alkyloxycarbonyl-n-pentyl)maleimides)—a comparative study

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The γ-transition temperature T_γ has been studied by differential thermal analysis in a series of 11 poly[N-(5-n-alkyloxycarbonyl-n-pentyl)maleimides] (PEMIS 5). Side chains containing even numbers of carbon from ethyl to n-docosyl were used. The γ-transition temperature decreases continuously as the number of methylene groups in the n-alkyl side chain increases. A method for estimating the T_γ of (–CH$_2$–) polyethylene (PE) was employed using γ-transition temperatures of an amorphous series of comb-like polymers with long n-alkyl side chains. The relationships between T_γ and chemical structures of comb-like polymers are discussed in terms of the number of participating groups within the movements of the n-alkyl side chain of the polymers. A comparative study has been made with some other comb-like polymers having oxy-n-alkyl moieties in the side chain, such as poly[N-(10-n-alkyloxycarbonyl-n-decyl)maleimides] (PEMIS 10), poly(n-alkylmethacrylates) (PAMAS) and poly(n-alkyl vinyl ethers) (PAVES). This internal motion is presumably made possible by the partial rotation of the various groups which link the side chains to the main chain of the comb-like polymers: for PAVES the link is the oxy-n-alkyl moiety; for PAMAS the link is a carboxy group; and for PEMIS 5 and PEMIS 10 the link is a carboxy-n-alkyl group. It is concluded that this transition is comb-like polymers with functional groups situated along the n-alkyl side chain is attributed to internal motions within the outer part of the n-alkyl side chain. Interactions with the main chain or with the neighbouring n-alkyl side chains belonging to adjacent structural units are therefore not important.

Keywords: comb-like polymers; γ-transition temperature; functional groups in comb-like polymers; poly[*N*-(5-n-alkyloxycarbonyl-n-pentyl)maleimides])

INTRODUCTION

Very recently Barrales-Rienda *et al.*[1,2] have interpreted the γ-transition temperature T_γ of five homologous series of comb-like polymers assuming that the T_γ of the n-alkyl side chain of a comb-like polymer satisfies the relationship

$$T_\gamma = \sum_i n_i T_{\gamma,i} \Big/ \sum_i n_i \qquad (1)$$

Thus, plots of $T_\gamma \sum_i n_i$ against n_i (where n_i represents the number of chemical groups capable of torsional oscillations, side-chain motions, conformational rearrangements, etc.) for these five homologous series gave in all cases very good straight lines. Although the least-squares slope for all the five series yields almost the same value for T_γ(–CH$_2$–), no special emphasis was put on the intercepts of the plots corresponding to poly(n-alkylmethacrylates) (PAMAS), poly(n-alkyl vinyl ethers) (PAVES) and poly[N-(10-n-alkyloxycarbonyl-n-decyl)maleimides] (PEMIS 10).

However, Barrales-Rienda *et al.*[2] studied the series of poly[N-(n-alkyl)maleimides] and applied equation (1); both the slope T_γ(–CH$_2$–) and intercept T_γ(–CH$_3$) agreed fairly well with those for the poly(1-alkylethylenes). They suggested that the mobility of an n-alkyl side chain in comb-like polymers, to an appreciable extent, is affected neither by the backbone structure nor by the attaching bridge or atom, although they may exhibit quite different main chains.

This interpretation is in reasonably good agreement with the molecular origin of secondary maxima given by Heijboer[3] as a side-group rotation around the bond linking it to the main chain. The model is based on rotations about the C–C bond for poly(1-alkylethylenes) or about the C–N bond for poly[N-(n-alkyl)maleimides] and assumes that the side group moves as a whole. In some cases and following Heijboer[3], it must be assumed that the deformation of adjacent valence angles often forces the main chain to partake slightly in the side-chain motion. This may not be excluded as a possibility in the case of poly(1-alkylethylenes), but it is very improbable in the case of poly[N-(n-alkyl)maleimides] because of the 2,5-dioxopyrrolidine-3,4-diyl residue, i.e. one being very flexible and the other semi-stiff. In other words, the genesis of the γ-transition temperature for comb-like polymers must be due exclusively to the side chains alone[1].

It was noted[1] that the contribution by the –CH$_3$ and –O– groups for poly(n-alkylmethacrylates) and poly(vinyl n-alkyl ethers) to the overall γ-transition temperature was about the same order, i.e. 419 ± 30 K and 384 ± 30 K, respectively. This was consistent with the assignment that was made.

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The mechanism of the n-alkyl side-chain motion of PEMIS 10 was considered[1] to be due to the motion of the outer part of the n-alkyl side chain from the oxy group –O– linked to the inner part of the n-alkyl side chain through the carboxyl group >C=O of the ester moiety.

In principle, the reason for the apparent discrepancies between the intercepts for PAMAS and PAVES may be due to the method employed to measure T_γ in poly[*N*-(10-n-alkyloxycarbonyl-n-decyl)maleimides]. In spite of the fact that thermal measurements extrapolated to zero rate of heating were used[2,4] to estimate T_γ, the true values may be slightly above the corresponding ones obtained by dilatometric techniques. From this point of view, the cooperative motion of the internal part of the n-alkyl side chain in PEMIS 10 cannot be completely excluded. It should probably explain the higher value of the intercept for PEMIS 10 in comparison with poly(n-alkylmethacrylates) and poly(n-alkyl vinyl ethers).

All these four homologous series of comb-like polymers have an oxy-n-alkyl chain in the side chain as a common feature. The aim of this study is to elucidate, at least from a qualitative point of view, this point by analysing a new series of comb-like polymers. For this reason a homologous series of poly[*N*-(5-n-alkyloxycarbonyl-n-pentyl)maleimides] was prepared. They have only five methylene groups in the inner part of the n-alkyl side chain. Poly[*N*-(5-n-alkyloxycarbonyl-n-pentyl) maleimides] (PEMIS 5) may be represented by the general chemical structure given in *Figure 1*.

Cowie *et al.*[5,6] have found that poly(di-n-alkyl itaconates) exhibit two glass transitions. These two transitions were detected in both dynamic and mechanical measurements and differential scanning calorimetry (d.s.c.). The higher temperature was associated with the conventional glass–rubber transition (T_g^u). The lower (T_g^l) was assigned to a separate relaxation process in the n-alkyl side chains.

Cowie *et al.*[7] have also found a third feature damping T_γ which is found in all comb-like polymers that contain methylene sequences of at least four carbon atoms (or the sequence –C–C–C–O–). The molecular origins of this low-temperature relaxation have been discussed[8].

Cowie *et al.*[9] have demonstrated that T_g^l has most of the characteristic of a 'conventional' glass transition rather than those of a subglass transition. They have also proposed a model which implies that T_g^l results from a cooperative movement of the whole side chain and not from a localized motion[7] of a few units such as at T_γ.

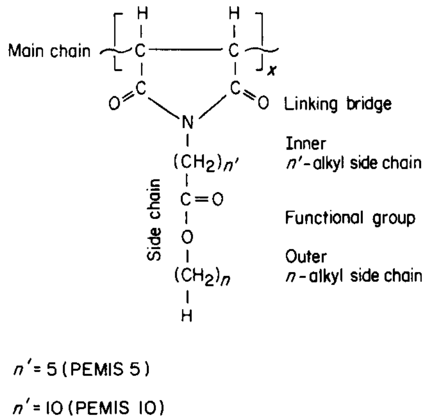


Figure 1 Structural unit of poly[*N*-(5-n-alkyloxycarbonyl-n-pentyl)maleimides] (PEMIS 5) and poly[*N*-(10-n-alkyloxycarbonyl-n-decyl)maleimides] (PEMIS 10)

EXPERIMENTAL

Materials

The synthesis of *N*-(5-n-alkyloxycarbonyl-n-pentyl)maleimides (EMIS 5) monomers from maleic anhydride, 6-aminocaproic acid and the respective n-alkyl bromides has been described elsewhere[10]. The homologous series of monomers was purified by recrystallization from petroleum ether. Data from t.l.c., elemental analysis and ^1H n.m.r. and i.r. spectra were in very good agreement with those expected from the chemical structure.

Polymerization and characterization

Polymers from EMIS 5 were obtained at 60°C by bulk free-radical polymerization using 2,2′-azobisisobutyronitrile (AIBN) as initiator. Polymers were isolated by pouring the solution into methanol, purified by fractional precipitation and dried in a vacuum oven at 40°C for 24 h to constant weight. Each of the polymers after the last purification was also examined by g.p.c., elemental analysis and by both ^1H n.m.r. and i.r. spectroscopy to verify the purity and structure of the samples. They were in agreement with the linear polymer structure and composition.

The g.p.c. chromatograms clearly showed that the polymer samples were free of monomers and that the molecular weight distributions were high enough to be in the range where their thermal properties are not dependent on molecular weight.

Thermal measurements

Thermal transitions were measured by means of a Du Pont 990 thermal analyser equipped with the Du Pont calorimeter cell. Temperatures down to $-120°C$ were attained by using a liquid-nitrogen attachment. This was taken as the starting temperature[4]. The heating rates employed were 10.0, 15.0, 20.0 and 25.0 K min^{-1}.

The subglass transition temperatures (T_γ) at each of the heating rates used were located as the temperature at the midpoint ($T_{1/2}$)[11]. Typical scanning curves for T_γ transition temperature of PEMI 5–8 obtained at different heating rates are shown in *Figure 2*. Values corresponding to $T_{1/2}$ have been gathered in *Table 1*. The magnitude and trend of the heat-capacity change in this region of PEMI 5–8 is similar not only to that in the γ-region of poly[*N*-(10-n-alkyloxycarbonyl-n-decyl) maleimides] (PEMIS 10) but also to those of low-crystallinity polyethylene[12] and of annealed polyoxyethylene[13].

Plots of log(sub-$T_g = T_\gamma$) vs. R_H for PEMIS are completely linear in all cases. They have been used to obtain values of T_γ at null rate of heating. The γ-transition temperature decreases continuously as the number of methylene groups in the n-alkyl side chain increases, as can be seen in the last column of *Table 1*.

The lower members of the series, i.e. from $n=2$ to $n=10$, show a glass transition temperature (T_g) by d.s.c., and the precise location of these glass transition temperatures has been obtained by a refractometric technique. The higher members of the series, i.e. from $n=12$ to $n=22$, present d.s.c. melting curves characteristic of comb-like polymers with crystallinity in the n-alkyl side chain. Apparent heats of melting (ΔH_f) have been obtained from the d.s.c. traces and melting point (T_m) by means of the same refractometric technique

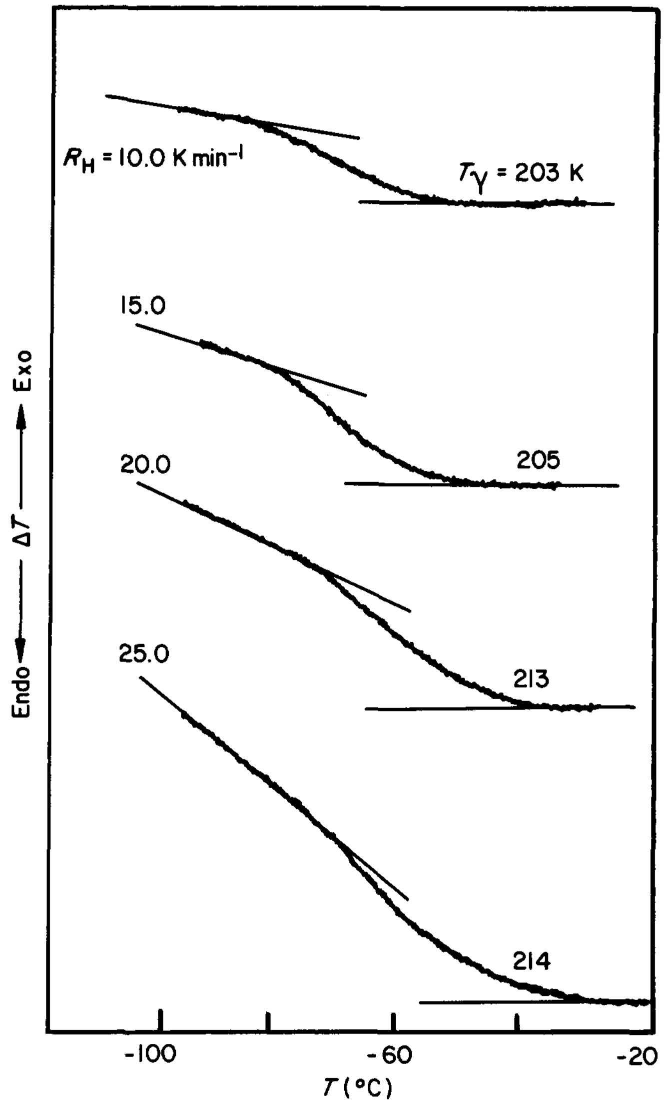


Figure 2 Comparison of the different thermal analysis traces of poly[N-(5-n-octyloxycarbonyl-n-pentyl)maleimide] (PEMI 5–8) at different heating rates as indicated. For the determination of the γ-transition temperature T_γ, the criterion of the midpoint $T_{1/2}$ was adopted (see 'Experimental' part)

Table 1 Summary of the values of secondary transition temperatures sub-$T_g = T_{1/2} = T_\gamma$ (K) (γ-transition temperature, T_γ) obtained by differential thermal analysis at several rates of heating (K min^{-1}) and extrapolated values ($T_{1/2}$ at $R_H \to 0$) at null rate of heating as a function of the number of methylene groups in the outer part of the n-alkyl side chain of a series of poly[N-(5-n-alkyloxycarbonyl-n-pentyl)maleimides] (PEMIS 5)

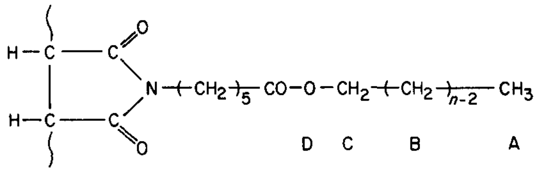
	$T_{\gamma,1/2}$ (K)[a]				
PEMIS	$R_H = 10.0$[b]	$R_H = 15.0$	$R_H = 20.0$	$R_H = 25.0$	$T_{\gamma,R_H \to 0}$
PEMI 5–22	146	158	167	178	127
PEMI 5–20	149	158	167	176	132
PEMI 5–18	163	172	182	193	144
PEMI 5–16	168	172	175	178	160
PEMI 5–14	185	196	205	219	162
PEMI 5–12	189	200	210	221	167
PEMI 5–10	183	190	194	196	175
PEMI 5–8	203	205	213	214	195
PEMI 5–6	207	212	213	215	205
PEMI 5–4	221	222	224	225	218
PEMI 5–2	241	244	244	244	241

[a] $T_{1/2}$ = midpoint temperature (see 'Experimental' part)
[b] Heating rates (R_H), expressed in K min^{-1}

employed also to locate T_g. Both series of experimental data will be analysed separately from those presented in the present paper and published in a forthcoming paper. Their analysis will be carried out in the usual way for some other poly(N-alkylmaleimides)[2].

DISCUSSION OF RESULTS

To apply relationship (1) to our homologous series of PEMIS 5, we first consider the different types of chemical groups in the outer part of the n-alkyl side chain, namely, the thermal methyl group, $-CH_3$, two types of methylene groups, $-CH_2-CH_2-CH_2-$ and $-O-CH_2-CH_2-$, and one type of ether group, $-CO-O-CH_2-$. They may be denoted A, B, C and D, respectively:



(2)

If methylene groups B and C are considered to be equivalent, their T_γ must be equal, i.e. $T_\gamma(B) = T_\gamma(C)$, and T_γ for the outer part of the n-alkyl side chain according to the above chemical formula (2) can be expressed as

$$(n+1)T_\gamma = [T_\gamma(A) + T_\gamma(D)] + (n-1)T_\gamma(B) \qquad (3)$$

If equation (3) is now used to plot values of T_γ for the series of PEMIS 5 given in *Table 1*, a linear plot results (*Figure 3*); the least-mean-squares method yields a slope of 147 K, which represents T_γ for a methylene group $-CH_2-$ such as those in the outer part of the n-alkyl side chain.

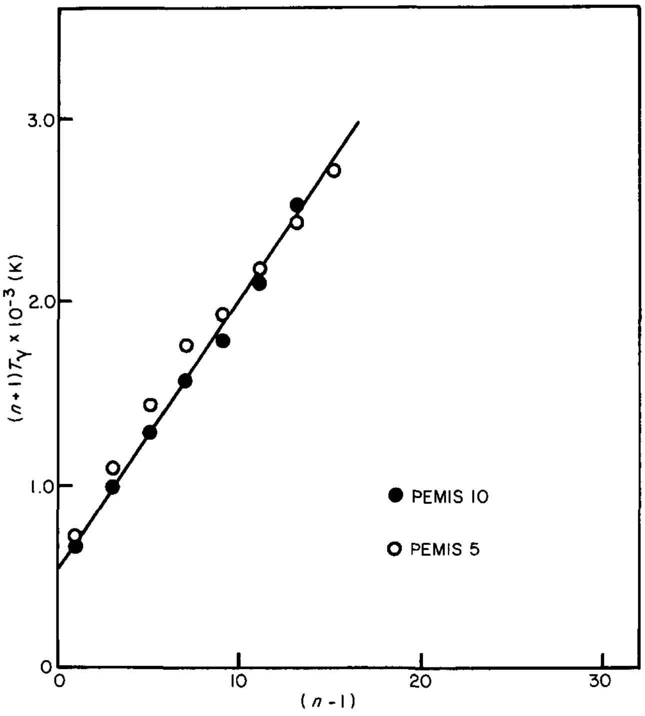


Figure 3 Dependence of the quantity $(n+1)T_\gamma$ on the number $(n-1)$ of methylene groups (without the terminal methyl) in the outer part of the n-alkyl side chain of poly[N-(5-n-alkyloxycarbonyl-n-pentyl) maleimides] (PEMIS 5) and poly[N-(10-n-alkyloxycarbonyl-n-decyl) maleimides] (PEMIS 10)

This value for T_γ agrees very satisfactorily with some others derived from other comb-like polymers exhibiting very different main chains[1,2]. Furthermore, on application of equation (1) to our comb-like PEMIS 5 as well as to PEMIS 10, considering the outer and the inner parts of the n-alkyl side chain and the functional group, the slope and the intercept give eccentric values for the γ-transition temperatures $T_\gamma(\text{–CH}_2\text{–})$, $T_\gamma(\text{–CH}_3)$ and $T_\gamma(\text{–O–})$ for the $\text{–CH}_2\text{–}$, –CH_3 and –O– groups, respectively. But if, in a similar manner, we plot on the same *Figure 3* the experimental data on PEMIS 10 described in previous publications[1,4], *Figure 3* will show that the polymers in these two series exhibit similar behaviour. We can see that the experimental data, as open and full circles, are distributed more or less at random, yielding almost the same slope and intercept. The agreement, as shown, seems to be quite satisfactory, in spite of the errors inherent to the experiment.

The intercept in *Figure 3* representing the contribution by the –CH_3 and –O– groups for PEMIS 5 and PEMIS 10 yields a value of 500 ± 30 K. In order to test the assumptions which were made with PEMIS 5 and PEMIS 10, some other homologues of comb-like polymers which included functional groups in the lateral n-alkyl side chain were examined by the same method.

On *Figure 4* we have plotted the data on poly(n-alkylmethacrylates) from Haldon and Simha[14] and those for poly(n-alkyl vinyl ethers) from Schell, Simha and Aklonis[15]. It should be made clear that the data quoted are indeed for a sub-T_g process and that these are associated[14,15] with molecular motions of the side chain. Both series of data are almost on the same straight line and yield a slope of 140 K and an intercept representing the contribution by the –CH_3 and –O– groups of 450 ± 30 K for poly(n-alkylmethacrylates) and poly(n-alkyl vinyl ethers). In *Figure 4* the location of $(n+1)T_\gamma$ vs. $(n-1)$ of poly(n-dodecylmethacrylate), $n = 12$, i.e. poly(laurylmethacrylate), is also given. A value of $T_\gamma = 149$ K has been estimated from dielectric measurements given by Kawamura *et al.*[16] (see Figure 19 of ref. 16).

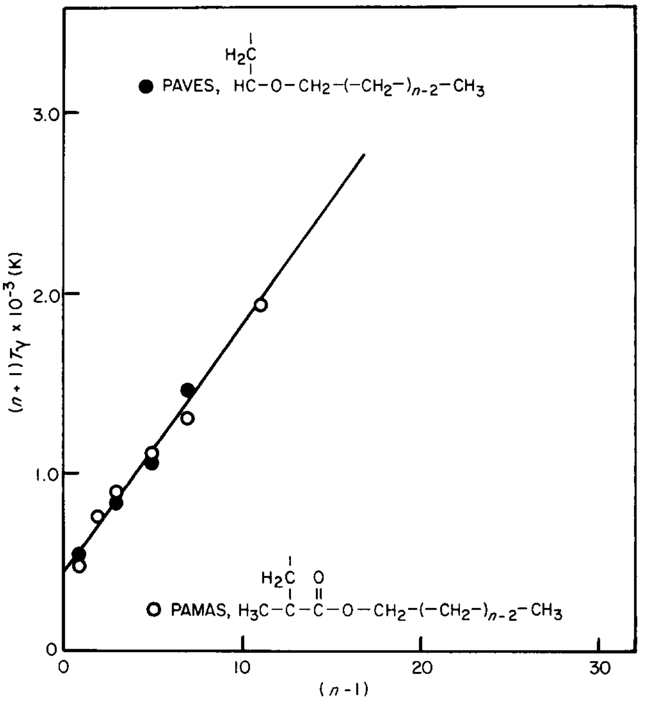


Figure 4 Dependence of the quantity $(n+1)T_\gamma$ on the number $(n-1)$ of methylene groups (without the terminal methyl) in the n-alkyl side chain of poly(n-alkylmethacrylates) and poly(n-alkyl vinyl ethers). T_γ represents γ-transition temperature

These values agree with those calculated for each separately[1], as mentioned in the introduction of this paper. The agreement between the calculated values for $T_\gamma(\text{–CH}_2\text{–})$ and $T_\gamma(\text{–CH}_3) + T_\gamma(\text{–O–})$ for this series of four comb-like polymers is quite good in spite of the procedure used to measure the T_γ transitions in PEMIS 5 and PEMIS 10. Although we have used for PEMIS 5 and PEMIS 10 in thermal measurements extrapolated to zero rate of heating, the estimated T_γ values may lie above the corresponding value obtained by dilatometric techniques employed to measure T_γ transitions in PAMAS[14], for instance.

From the plots in *Figure 3* and *Figure 4* we conclude that the γ-transition temperature T_γ in poly[*N*-(10-n-alkyloxycarbonyl-n-decyl)maleimides] (PEMIS 10) and poly[*N*-(5-n-alkyloxycarbonyl-n-pentyl)maleimides] (PEMIS 5) arises from the outer part of the n-alkyl side chain including only the oxy group (–O–) attached to the next carboxy one (–CO–). This finding is in agreement with the conclusion advanced by Shimizu *et al.*[17] that comb-like polymers exhibit γ-relaxations if they possess sequences –C–C–C–C– or –O–C–C–C– in the side chain and the rotation of central –C–C– bonds in this sequence is not hindered by the main chain[8]. In most respects this explains well the γ-transition in poly(n-alkyl vinyl ethers) where the carboxy group (–CO–) is absent and to a certain extent it explains the same transition in poly(n-alkylmethacrylates) where the oxy-n-alkyl side chain $\text{–O–(–CH}_2\text{–)}_n\text{–H}$ is directly connected to the main chain by a carboxy group –CO–. The influence of the main chain for both polymers cannot be ruled out. However, the investigation of PEMIS 5 and PEMIS 10 and their simultaneous analysis carried out in the present paper has revealed an interesting behaviour which has not been observed in any other comb-like polymers to date. For these two homologous series, the functional group is situated far away from the main chain, so the only plausible explanations must be not only the steric hindrance introduced by the carboxy group –CO– on its own n-alkyl side chain but also the interactions and steric hindrances with the neighbouring n-alkyl side chains belonging to adjacent structural units.

For this reason, the nature of the n-alkyl side chain of a carboxy group –CO– exerts a strong influence on the dependence between the γ-transition temperatures and the length of the inner part of an n-alkyl side chain in comb-like polymers. It can be concluded for our PEMIS 5 and PEMIS 10 that the carboxyl group may sterically hinder rotation and other motions along the inner n-alkyl side chain.

The value obtained for $T_\gamma(\text{–CH}_2\text{–})$ for PEMIS 5, i.e. T_γ for the methylene groups $\text{–CH}_2\text{–}$ with methylene neighbours, agrees quite well not only with T_γ data derived from some other comb-like polymers[1,2] but also with T_γ data for PE as determined by different procedures and different authors[12,18–22], with T_γ for polyoxyethylene[13] and with $T_\gamma(\text{–CH}_2\text{–})$ data derived using equation (1) for polymers containing methylene units in the backbone[2,23] (see Table 3 of ref. 2).

All this strongly supports the validity of equation (1) when it is applied to comb-like polymers such as PEMIS

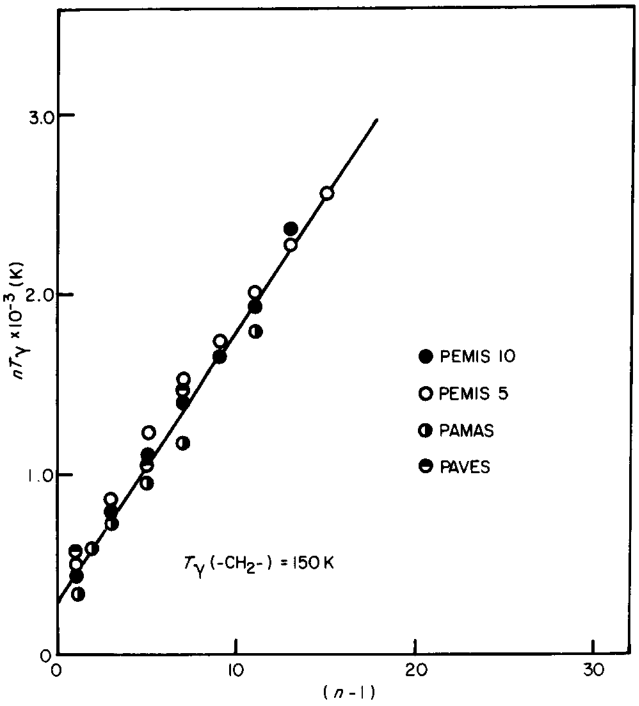


Figure 5 Dependence of the quantity nT_γ on the number $(n-1)$ of methylene groups (without the terminal methyl) in the outer part of the n-alkyl side chain of poly[*N*-(10-n-alkyloxycarbonyl-n-decyl)maleimides] (PEMIS 10) and poly[*N*-(5-n-alkyloxycarbonyl-n-pentyl)maleimides] (PEMIS 5), or methylene groups (without terminal methyl) in the n-alkyl side chain of poly(n-alkyl methacrylates) (PAMAS) and poly(n-alkyl vinyl ethers)(PAVES). For PAVES for ether linkage has been included in the quantity nT_γ

5 and PEMIS 10 as well as the adequacy of labelling our sub-T_g as a true γ-transition temperature. However, when equation (1) is applied to poly(di-n-alkyl itaconates) data from Cowie *et al.*[5,6], neither the slope nor the intercept yield reasonable values for $T_\gamma(-CH_2-)$ and $T_\gamma(-CH_3)+T_\gamma(-O-)$.

Nevertheless, from the results we have derived, we must realize that the denomination and mechanism for the existence of sub-$T_g = T_\gamma$ (or T_g^1 as in the paper by Cowie *et al.*[9]) in the comb-like polymers studied in the present paper can be speculative. The Reneker effect[24], the Pechhold 'kink block' movement[25], crankshaft motions of Schatzki[26] and Boyer[27], the 'flip-flop' motion of Boyd and Breitling[28], and the cooperative-type movement of the whole side-chain model of Cowie[9] (attributed to T_g^1 as a 'conventional' glass transition temperature) are all descriptive of n-alkyl side-chain motions and are independent of the main chain.

Finally, we would like to mention that the contribution of the oxy group in equation (1) and as a consequence in equations (3) and (4) may be small if not non-existent because the oxy group attached to the carboxy (i.e. the carbonyl carbon–ester oxygen) is highly restricted in its motion. Its exclusion from equations (1), (2) and (3) does not introduce big differences in the values obtained for $T_\gamma(-CH_2-)$ from the four series of comb-like polymers studied in the present paper (see *Figure 5*). We believe that the present results are not in disagreement with those obtained by Cowie *et al.*[7,9] and their own interpretations but also they represent a new contribution to a better understanding of the transitions taking place in the n-alkyl side chain of comb-like polymers.

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