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Influence of a Functional Group Situated along the Side Chain on Side-Chain Crystallinity and on the Heat and Entropy of Melting of Comblike Poly[*N*-((*n*-alkyl(oxycarbonyl))methyl)maleimides] and Poly[*N*-(5-(*n*-alkyl(oxycarbonyl))-*n*-pentyl)maleimides]

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ABSTRACT: Thermodynamic properties of poly[*N*-((*n*-alkyl(oxycarbonyl))methyl)maleimides] (PEMIs 1) containing 14–22 carbon atoms and poly[*N*-(5-(*n*-alkyl(oxycarbonyl))-*n*-pentyl)maleimides] (PEMIs 5) containing 12–22 carbon atoms, in the outer part of the lateral *n*-alkyl side chain were studied by means of differential scanning calorimetry and a refractometric technique. The influence of an ester group situated along the lateral *n*-alkyl side chain on the crystallization of the side chains was studied. The thermal properties of these two homologous series of comblike polymers were compared to those of poly[*N*-(10-(*n*-alkyl(oxycarbonyl))-*n*-decyl)maleimides] (PEMIs 10) because of strong similarities in properties and structure. The enthalpic data for these three series (PEMIs 1, PEMIs 5, and PEMIs 10) show that only a part of the outer *n*-alkyl side chain is present in the crystallization. The thermal properties and thermodynamic characteristics appear to be adequately described by a basic model similar to that for the PEMIs 10 series. The contributions to the heat and entropy of melting per methylene group show that the hexagonal paraffinlike crystal modification is present in the PEMIs 1 and PEMIs 5 series, in good agreement with X-ray diffraction data for the same compounds. There exist for the three homologous series good linear correlations between the critical chain length in the outer part of the *n*-alkyl side chain needed to initiate the crystallization and the term $\Delta H_{t,e}$ due to the chain-end contribution to the melting enthalpy.

Introduction

This article discusses the results of an extension to PEMIs 1 and PEMIs 5 of a previous calorimetric study of PEMIs 10.

It has been well established that polymers with long *n*-alkyl side chains crystallize. Only in a few cases has a quantitative determination of the degree of crystallinity of these comblike polymers been made. Some authors have measured the heat of melting, the melting temperatures, the derived entropies of melting and, in a few cases, the degree of crystallinity. Dependence of the thermodynamic properties and/or degree of crystallinity on *n*-alkyl side chain length has been examined for atactic poly(1-alkyl acrylates),[1] poly(1-alkyl acrylamides),[2] poly(1-alkyl vinyl esters),[1,2] poly(1-alkyl methacrylates),[3,4] poly(di-*n*-alkyl itaconates),[5] poly[*N*-(*n*-alkyl)maleimides],[6] poly[*N*-(10-(*n*-alkyl(oxycarbonyl))-*n*-decyl)maleimides][7] (PEMIs 10), stereoregular and atactic poly(1-alkylethylenes),[8,9,10] stereoregular and atactic poly(1-alkylethylene oxides),[10,11] and poly(γ-*n*-alkyl L-glutamates).[12] Almost all authors have reached the conclusion that the part of the *n*-alkyl side chain extending beyond eight methylene groups participates in the crystallization.

It was of interest to study the influence of a functional group situated along the *n*-alkyl side chain on the crystallinity and thermodynamic properties of comblike polymers with long *n*-alkyl side chains. Consequently, a study of the homologous series of PEMIs 1 and PEMIs 5 was undertaken. They have one and five methylene groups in the inner part of the *n*-alkyl side chain, respectively.

There are two fundamental aspects to the present work: (1) to show the influence of the length of the outer part of the *n*-alkyl side chain within each of the two homologous series of PEMIs 1 and PEMIs 5 independently on the crystallization and heat and enthalpy of melting and (2) to discover the role played by the functional group situated along the *n*-alkyl side chain or the inner part of the *n*-alkyl side chain of the three homologous series of PEMIs 1, PEMIs 5, and PEMIs 10 on the estimated values of some characteristic thermodynamic parameters.

The structural unit of the comblike polymers that will be studied in the present paper may be represented by the simplified chemical structure given in Figure 1.

Our three homologous series of comblike polymers, PEMIs 1, PEMIs 5, and PEMIs 10, have as a main feature an ester group situated along the *n*-alkyl side chain. Be-

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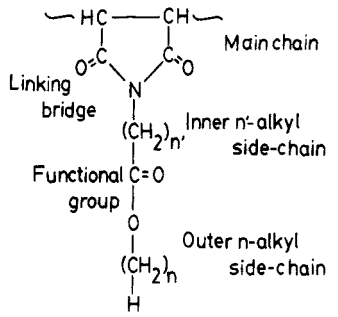

PEMIS 1, n'= 1 and n= 14 to 22

PEMIS 5, n'= 5 and n= 12 to 22

PEMIS 10, n'= 10 and n= 12 to 22

Figure 1. Structural unit of poly[*N*-((*n*-alkyl(oxycarbonyl))-methyl)maleimides] (PEMIs 1), poly[*N*-(5-(*n*-alkyl(oxycarbonyl))-*n*-pentyl)maleimides] (PEMIs 5), and poly[*N*-(10-(*n*-alkyl(oxycarbonyl))-*n*-decyl)maleimides] (PEMIs 10).

sides, as has been checked by X-ray diffraction, crystallization does not begin until a minimum length is achieved in the outer part of this *n*-alkyl side chain,[13,14] i.e., a certain *n*-alkyl length from the ester group and not from the main chain, as in the case of comblike polymers without functional groups in the *n*-alkyl side chain.

Experimental Section

Materials. The *N*-((*n*-alkyl(oxycarbonyl))methyl)maleimides (EMIs 1) and *N*-(5-(*n*-alkyl(oxycarbonyl))-*n*-pentyl)maleimides (EMIs 5) monomers were prepared from maleic anhydride with glycine and 6-aminocaproic acid, respectively.[15] Polymers were obtained by bulk free radical polymerization at 60 °C and by using 2,2'-azobis(isobutyronitrile) (AIBN) as initiator. After completion of polymerization, polymers were isolated by precipitation upon pouring into methanol and then they were purified by fractional precipitation and dried under vacuum at 40 °C to constant weight.

Each polymer after final purification was also examined by GPC, by elemental analysis, and by both ^{1}H NMR and IR spectroscopy to verify the purity and structure of the samples. These were in agreement with the linear polymer structure and composition.

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

Thermal Measurements. Calorimetric measurements were made in a Du Pont 900 thermal analyzer equipped with a Du Pont calorimeter cell. Other experimental details have been given elsewhere.[7] DSC traces that were used to obtain apparent melting enthalpies are given in Figure 2.

Refractometric Technique. In order to obtain more reliable values for the melting point temperature, the refractometric technique was employed. This technique, from the point of view of its execution, has shown some advantages for the localization of glass transition temperatures in these two series of comblike polymers.[16]

Typical plots to obtain melting point temperatures are given in Figure 3, which show the dependence of the refractive index with temperature. The melting temperature is defined by the point of intersection of the extrapolated curve with the linear part of the graph. The melting point temperatures so obtained are considered to be very near those obtained at rates as low as the ones normally used in dilatometric measurements.

Results and Discussion

Table I lists the calorimetric and refractometric melting temperatures of PEMIs 1 and PEMIs 5. The melting temperatures obtained from refractometric measurements are only slightly higher than those ones obtained by calorimetry. The melting entropies, included as the last column in Table I, were calculated with the usual relationship $\Delta S_f = \Delta H_f/T_m$, where T_m is the refractometric melting temperature. Consequently, all the calculated entropies are almost true values, since T_m represents a melting temperature near the equilibrium melting point. This may be sufficient for our purposes.

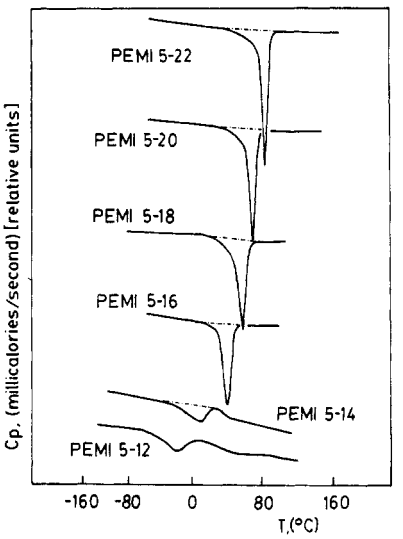

Figure 2. Comparison of DSC melting curves for a homologous series of crystalline poly[*N*-(5-(*n*-alkyl(oxycarbonyl))-*n*-pentyl)-maleimides] (PEMIs 5) as indicated. Experimental conditions: scan rate, 5 K/min; attenuation selector setting, 8 mcal/s; chart rate, 10 K/mm. The endotherms have not been normalized, so the relative areas of the endotherms do not correspond to equivalent amounts of sample in all cases. Specimens weighing 18–25 mg have been used.

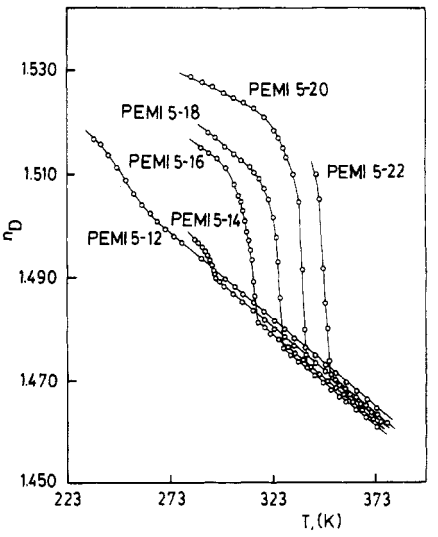

Figure 3. Dependence of the refractive index n_D on temperature for a series of crystalline poly[*N*-(5-(*n*-alkyl(oxycarbonyl))-*n*-pentyl)maleimides] (PEMIs 5). A heating rate of 1/30 K/min was employed.

It is well-known that melting points of compounds containing *n*-alkyl chains converge to an unique value. When the paraffinlike chain is infinitely long, this melting point should correspond to that of a crystal of completely extended chains of linear polymethylene. The relationship between T_m and n, the number of methylene groups in the *n*-alkyl chain, assuming the linearity of the enthalpy and the entropy,[17,18] is

$$T_m = (\Delta H_{f,e} + \alpha n)/(\Delta S_{f,e} + \beta n) = T_m^0(n + a)/(n + b) \quad (1)$$

Table I
Apparent Heat of Melting (ΔH_f), Melting Transition Temperature (T_m) and Entropies of Melting (ΔS_f) for Three Series of PEMIs 1, PEMIs 5, and PEMIs 10 Exhibiting Crystallinity in the *n*-Alkyl Side Chain

compd	ΔH_f,[a] cal/(mol structural unit)	T_m, K DSC[c]	T_m, K refractometry[d]	ΔS_f,[b] cal/(mol K)
PEMI 1-22	7351.6	346.7	345.2	21.3
PEMI 1-20	5924.6	337.2	336.2	17.6
PEMI 1-18	3924.2	320.2	323.2	12.1
PEMI 1-16	2177.1	290.2	303.7	7.2
PEMI 1-14	1256.3	268.2	289.2	4.3
PEMI 5-22	8122.3	348.5	350.7	23.2
PEMI 5-20	6557.3	338.2	339.2	19.2
PEMI 5-18	4468.8	326.9	328.2	13.6
PEMI 5-16	3263.0	313.8	315.2	10.4
PEMI 5-14	2112.6	283.2	295.2	7.2
PEMI 5-12			273.2	
PEMI 10-22	9852.0	339.0	340.2	28.9
PEMI 10-20	8390.1	330.0	339.2	24.7
PEMI 10-18	6756.5	321.0	331.2	20.4
PEMI 10-16	5495.1	312.0	324.2	17.0
PEMI 10-14	3848.2	297.0	312.2	12.3
PEMI 10-12	2357.3	275.0	298.2	7.9

[a] Values of ΔH_f and T_m by DSC for PEMIs 10 have been taken from ref 7. [b] Values of ΔS_f have been calculated with values of T_m estimated by refractometry. [c] At 5 K/min. [d] At 1/30 K/min.

Table II
Values of the Parameters Calculated by Mean Least-Squares Curve Fitting to Eq 1 for the Refractometric Melting Points (T_m) and Entropies ($\Delta H_f/T_m$) of PEMIs 10, PEMIs 5, and PEMIs 1

homologous series	T_m^0, K	a	b	ΔS_{fe}, cal/(mol K)	β, cal/(mol $-CH_2-$ K)
PEMIs 10	406.0	−3.85	−0.79	−16.82	2.08
PEMIs 5	408.0	−7.76	−5.53	−22.00	2.04
PEMIs 1	408.0	−8.29	−5.72	−27.46	2.22

where α is the enthalpy of melting per mole of methylene groups, $\Delta H_{f,e}$ is the contribution due to the chain ends, β represents the contribution of each added methylene group to the entropy of melting, and $\Delta S_{f,e}$ is the contribution of the chain ends. T_m^0 is the limit temperature, and a and b are two constants. This equation can be applied only to crystals of the same geometry.

While it is well recognized that the linearity of the enthalpy of melting with the chain length can safely be accepted, linearity of the entropy of melting is another matter.[18,19]

Equation 1 was applied to our refractometric melting point data included in the fourth column of Table I for PEMIs 1, PEMIs 5, and PEMIs 10. The values of the parameters T_m^0, a, and b for each one of the homologous series were obtained by least squares curve fitting and are collected in Table II. As can be seen, the different values of T_m^0 calculated agree fairly well with the value of 408.0 K estimated by Jordan[20] for poly(*n*-alkyl acrylates) and by Barrales-Rienda et al.[6] for poly[*N*-(*n*-alkyl)maleimides] and with values calculated for some other oligomeric systems including *n*-alkanes from data compiled by Broadhurst.[17]

In Figure 4 we have represented the experimental refractometric melting points against the number of methylene groups in the outer part of the *n*-alkyl side chain collected from Table I for PEMIs 1, PEMIs 5, and PEMIs 10. The full lines have been drawn with the values of T_m^0, a, and b from Table II. Although the limit temperature is known for PE with hexagonal packing, the value of 408.0 K for T_m^0 is almost the same as that found by Jordan[20] by extrapolation of the limiting free energy of melting vs. temperature curves given for hexagonal *n*-alkanes by Atkinson and Richardson.[21]

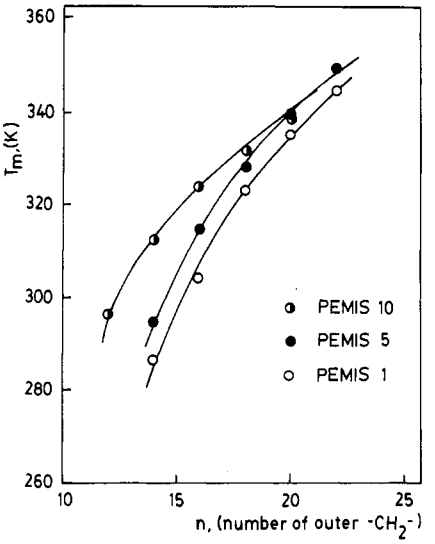

Figure 4. Plots of melting point temperatures against the number of methylene groups in the outer part of the *n*-alkyl side chain (including terminal methyl) of a series of crystalline PEMIs 1, PEMIs 5, and PEMIs 10. Experimental points for T_m have been measured by means of a refractometric technique. Full lines represent calculated values according to eq 1 and using values of the parameters obtained by a least-squares curve fitting to eq 1.

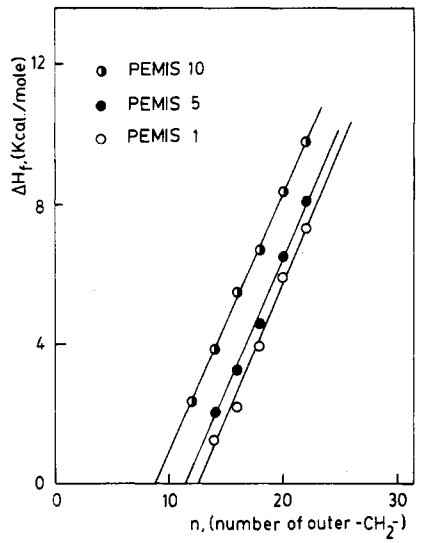

Figure 5. Plots of the apparent melting enthalpy ΔH_f against the number n of methylene groups (including terminal methyl) in the outer part of the *n*-alkyl side chain of three homologous series of crystalline PEMIs 1, PEMIs 5, and PEMIs 10. These plots have been used to obtain the number of critical methylene groups n_a needed to initiate the crystallization in the *n*-alkyl side chain and some other characteristic thermal parameters.

Broadhurst[17] has fit the melting enthalpies of a series of *n*-alkanes in the hexagonal modification to an equation of the form proposed by Flory and Vrij[19]

$$\Delta H_f = \Delta H_{f,e} + \alpha n \quad (2)$$

where each of the parameters has the same meaning as in eq 1. Plots of apparent melting enthalpies vs. the number of methylene groups including the terminal methyl in the outer part of the *n*-alkyl side chain n for PEMIs 1, PEMIs 5, and PEMIs 10 are given in Figure 5. Enthalpic contribution due to chain ends values $\Delta H_{f,e}$ and enthalpies of melting per mole of methylene group values for these three series and for some other comblike polymers are listed in

Table III
Values of the Parameters ΔH_{fe} and α of Eq 2 and n_a' of Eq 7 for Different Homologous Series of Comblike Polymers

homologous series	ΔH_{fe}, cal/mol	α, cal/(mol $-CH_2-$)	n_a'	ref
poly(1-*n*-alkylethyl oxides)	-5503.1	733.7	7.5	10
poly(1-*n*-alkyl ethylenes)	-6236.8	733.7	8.5	10
poly[*N*-(10-(*n*-alkyl(oxycarbonyl))-*n*-decyl)maleimides]	-6676.9	752.7	8.7	7
poly(*n*-alkyl acrylates)	-7271.0	791.6	9.2	1
poly(*n*-alkyl vinyl esters)	-7686.0	829.5	9.3	1
poly[*N*-(*n*-alkyl)maleimides]	-8206.4	766.6	10.4	6
poly[*N*-(5-(*n*-alkyl(oxycarbonyl))-*n*-pentyl)maleimides]	-8877.6	765.6	11.6	this work
poly[*N*-(*n*-alkyl)acrylamides]	-9262.0	774.8	12.0	1
poly[*N*-((*n*-alkyl(oxycarbonyl))methyl)maleimides]	-10217.6	796.9	12.8	this work

Table IV
Estimation of the Side-Chain Crystallinity of Two Homologous Series of PEMIs 1 and PEMIs 5

compd	MW (outer part *n*-alkyl side chain)	Crystallinity X_c eq 3	Crystallinity X_c' eq 9	f	$X_{cs} = fX_c$	no. crystalline $-CH_2-$ in outer part of *n*-alkyl side chain n_c eq 5	no. crystalline $-CH_2-$ in outer part of *n*-alkyl side chain n_c' eq 8	no. amorphous $-CH_2-$ in outer part of *n*-alkyl side chain n_a eq 6	no. amorphous $-CH_2-$ in outer part of *n*-alkyl side chain n_a' *q* 7
PEMI 1-22	308.6	0.35	0.28	1.30	0.45	10.0	9.2	12.0	12.8
PEMI 1-20	280.5	0.26	0.23	1.55	0.40	8.1	7.2	11.9	12.8
PEMI 1-18	252.5	0.18	0.18	1.61	0.30	5.3	5.2	12.7	12.8
PEMI 1-16	224.4	0.11	0.12	1.69	0.19	3.0	3.2	13.0	12.8
PEMI 1-14	196.4	0.07	0.05	1.79	0.12	1.7	1.2	12.3	12.8
PEMI 5-22	308.6	0.30	0.28	1.68	0.50	11.1	10.4	11.0	11.6
PEMI 5-20	280.5	0.25	0.24	1.75	0.45	8.9	8.4	11.1	11.6
PEMI 5-18	252.5	0.18	0.19	1.84	0.34	6.1	6.4	11.9	11.6
PEMI 5-16	224.4	0.14	0.14	1.94	0.28	4.4	4.4	11.6	11.6
PEMI 5-14	196.4	0.10	0.08	2.08	0.22	2.9	2.4	11.1	11.6
PEMI 5-12	168.3		0.01				0.4		11.6

Table III. Values for α agree with that of 735 cal/mol of $-CH_2-$ corresponding to *n*-alkanes[17] and to some other comblike polymers having long side chains.[1] There are two methods to calculate the degree of crystallinity of comblike polymers.[1,7] The degree of crystallinity X_c is given by

$$X_c = \Delta H_f/\Delta H_{f,0} = [n\Delta H_f(\text{methylene groups})/(\Delta H_{f,e} + n)] \quad (3)$$

where $\Delta H_{f,0}$ represents the melting enthalpy of the pure crystalline phase. The crystallinity of the side chains is

$$X_{cs} = fX_c = X_c[\Delta H_f(\text{structural unit})/n\Delta H_f(\text{methylene groups})] \quad (4)$$

The number of crystalline and amorphous methylene groups are respectively

$$n_c = nX_{cs} \quad (5)$$

and

$$n_a = n - n_c \quad (6)$$

Values of these quantities are listed in Table IV.

A second procedure is based on the assumption that a plot of ΔH_f vs. n gives a straight line as shown in Figure 5. When $\Delta H_f = 0$, i.e., $\Delta H_f = C + k'n = 0$, the number of crystalline and amorphous methylenes groups are respectively

$$n'_a = C/k' \quad (7)$$

$$n'_c = n - n'_a \quad (8)$$

and the degree of crystallinity

$$X'_c = 14.026\ (n - n'_a)/\text{MW(structural unit)} \quad (9)$$

Values calculated according to this second procedure are also gathered in Table IV and as can be seen are practically identical with those calculated by the first approach. The values obtained by these two procedures will yield the same value for the crystalline fraction. This is true, as can be seen from data in Table IV. However, this agreement between both procedures is attained only if we consider the outer part of the *n*-alkyl side chain.

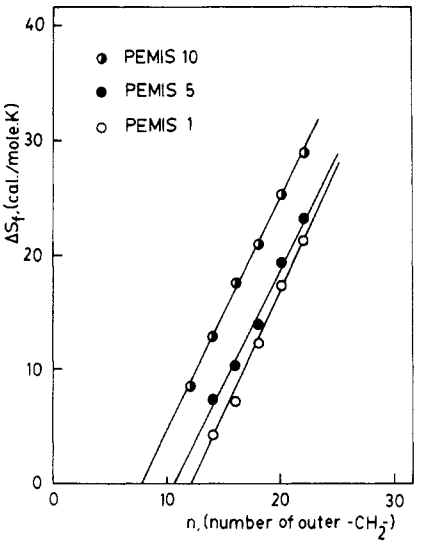

Figure 6. Plots of the melting enthalpy ΔS_f against the number n of methylene groups (including terminal methyl) in the outer part of the *n*-alkyl side chain of three homologous series of crystalline PEMIs 1, PEMIs 5, and PEMIs 10 to obtain some characteristic thermal parameters. Good linearity between ΔS_f and n can be easily observed.

We have also found that a plot of ΔS_f from values given in the last column of Table I against n satisfies well the relation

$$\Delta S_f = \Delta S_{f,e} + \beta n \quad (10)$$

as can be seen in Figure 6. The parameters $\Delta S_{f,e}$ and β have the same meaning as in expression 1. The values of $\Delta S_{f,e}$ and β in eq 10 are collected for PEMIs 1, PEMIs 5, and PEMIs 10 in Table II. Both series of values for $\Delta S_{f,e}$ and β are close to those for some other comblike polymers.[1]

Comblike polymers have abnormally high values for the enthalpy $\Delta H_{f,e}$ because of their end group contribution, as can be seen in Table III. This fact can be as a consequence of the n-alkyl side-chain anchorage to the main chain. Comparing columns second and fourth, one notes that this energy is clearly related to the necessity of reaching a minimum length in order that the crystallization would appear, i.e., the number of amorphous methylene groups. In the present case, this fact reveals the influence of the main chain as well as the linking bridge on the critical length to crystallize. As can be seen, there exist a very good correlation between $\Delta H_{f,e}$ and n'_a.

Finally it is useful to draw some conclusions concerning the influence of the location of ester group upon the crystallization, especially from the point of view of the number of methylenes in the inner alkyl side chain. From Table III, the following sequence of n'_a for the different PEMIs is obtained:

$$\text{PEMIs 10} < \text{PMIs 5} < \text{PMIs 1}$$
$$n'_a = 8.9 \quad n'_a = 11.6 \quad n'_a = 12.8$$

Comparison of PEMIs 1, PEMIs 5, and PEMIs 10 lead to the conclusion that for more inner methylenes between the ester group and the main chain fewer outer methylene groups are required to initiate crystallization; in other words the ester group controls the appearance of the crystallinity as well as its situation with respect to the main chain.

Concluding Remarks

The conclusions reached in this paper confirm those advanced[7] for PEMIs 10. It can be summarized that only a part of the outer n-alkyl side chain participates in the crystallization. Thus, crystallization of the inner part of the side chain is hindered by the main chain as well as by the ester group, because its size prevents the side-chain packing of the inner part of the n-alkyl side chain in the typical hexagonal arrays of comblike polymers. Consequently, it is necessary to reach a critical chain length within the external part of the side chain to initiate crystallization. This length is similar to that obtained for many other comblike polymers where the functional group lie near the main chain.

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Registry No. PEMI 1-22, 108292-39-3; PEMI 1-20, 108292-41-7; PEMI 1-18, 108292-43-9; PEMI 1-16, 108292-45-1; PEMI 1-14, 108292-47-3; PEMI 5-22, 108292-49-5; PEMI 5-20, 108292-51-9; PEMI 5-18, 108292-53-1; PEMI 5-16, 108292-55-3; PEMI 5-14, 108292-57-5; PEMI 5-12, 108292-59-7; PEMI 10-22, 73599-08-3; PEMI 10-20, 73593-01-8; PEMI 10-18, 73593-03-0; PEMI 10-16, 73593-05-2; PEMI 10-14, 73593-07-4; PEMI 10-12, 73593-09-6.

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Conformational Characteristics of Phthalic Acid Based Polyesters

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ABSTRACT: Dielectric measurements were performed on solutions of poly(diethylene glycol phthalate) (PDEP) in benzene at different temperatures. The value of the dipole moment ratio, in terms of which the dielectric results were expressed, changed from 0.637 to 0.679 in the temperature interval 30–60 °C. Conformational energy calculations indicated that when the two ester groups of phthaloyl residue are coplanar to the phenyl group, the interaction energy is strongly repulsive; however, the energy becomes attractive when the rotational angles about C^{Ph}–C* bonds place the ester groups on a plane perpendicular to the phenyl group. By use of the information derived from these calculations, a three-rotational-state model gave values of the dipole moment and its temperature coefficient in good agreement with the experimental results.

Introduction

The critical interpretation of the dielectric and thermoelastic properties of poly(diethylene glycol terephthalate) (PDET) has been useful to obtain information on the conformational characteristics of these chains.[1-3] These studies seem to suggest that gauche states about CH_2–CH_2 bonds, which give rise to first-order 0···0 interactions, are significantly more favored than similar states

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