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Miscibility in blends of stereoregular poly(methyl methacrylate)/poly(ethylene oxide) based oligomers

L. Hamon[a], Y. Grohens[b,*], A. Soldera[c], Y. Holl[a]

[a]Institut de Chimie des Surfaces et Interfaces, CNRS UPR 9069, 15, rue J.Starcky, BP 2488 Mulhouse cedex, France
[b]Laboratoire de Biologie et Chimie Moléculaires, Centre de Recherche, Rue Saint-Maudé, 56325 Lorient cedex, France
[c]CEA-DAM, Centre d'Etudes du Ripault, DCDM/MS, BP 16, 37260 Monts, France

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Abstract

The miscibility of blends of poly(methyl methacrylate), PMMA, and poly(ethylene oxide), PEO, oligomers was studied by temperature-modulated DSC as a function of the PMMA stereoregularity, the molecular weight and the nature of the chain ends of the PEO. The Flory–Huggins interaction parameter $\chi_{1,2}$ was determined using the methodology developed by Kim and Burns and compared to those calculated from the Hildebrand solubility parameters drawn from the Van Krevelen tables. First, it turns out that the miscibility domain is larger for the a- and s-PMMA than for the isotactic isomer (as shown in previous studies) and, moreover, larger for butyl terminated PEO oligomers. The Flory–Huggins interaction parameter $\chi_{1,2}$ decreases with the increase of the PEO molecular weight as well as with the syndiotacticity of the PMMA and is lower for the PEO with alkyl modified chains ends. These results highlight the non negligible contribution of the free volume to the interaction parameter and also the importance of the kinetic of the PEO crystallisation on the phase separation process. © 2001 Published by Elsevier Science Ltd.

Keywords: Polymers; Miscibility; Oligomers

1. Introduction

Several studies have been made on blends of poly(ethylene oxide), PEO, and poly(methyl methacrylate), PMMA, in the last decades [1–10]. Numerous works reported that the miscibility domain ranges between 10 and 30% of PEO by weight depending on the PMMA tacticity or molecular weight [1–6]. No phase diagram is available yet in the literature and the UCST [7] or LCST [8] behaviour of the PMMA/PEO blend with temperature is still contradictory. This is due to the partially miscible nature of the blend due to the occurrence of PEO crystallisation for rather low contents, namely, 20–30%. It is often concluded that for that system the transition between homogeneous and heterogeneous blends corresponds to the appearance of the crystallinity in the mixture [9–12].

PMMA stereoregularity is one of the major factor affecting the miscibility of the blend with PEO. Thus, a- and s-PMMA/PEO systems are miscible at the molecular level in the amorphous state whereas highly isotactic PMMA give rise to a phase separation even at low PEO content [1,13]. Below the melting point of PEO or at concentration at which the PEO crystallises, it was concluded from small-angle X-ray scattering (SAXS), that amorphous a- or s-PMMA is incorporated between the crystalline PEO lamellae, whereas i-PMMA is rejected to the interfibrillar PEO spherulite region [1,4,13].

The interaction between the two polymers is generally claimed to be weak, possibly in the order of the van der Waals type interaction [1,9,14]. Specific interactions between the carbonyl carbon atoms of the PMMA and the oxygen atoms of PEO were suggested from vibration spectroscopy investigations [15]. However, the exact nature of these interactions is still unknown. The Flory–Huggins $\chi_{1,2}$ interaction parameter is generally close to zero and is in some cases reported to be positive [7] or negative [8] depending upon temperature and composition. Moreover, as pointed out by Ito et al. [16] the enthalpic contribution to $\chi_{1,2}$ is expected to be much smaller than the entropic one.

This influence of the entropic contribution is supported by the fact that conformational changes can occur in PEO due to the mixture with PMMA. Indeed, it was concluded from IR investigations that the interaction with PMMA forces PEO to adopt a planar ttt conformation whereas its conformation in the bulk crystalline state is mainly helicoidal

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* Corresponding author.
E-mail address: yves.grohens@univ-ubs.fr (Y. Grohens).

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[9,15]. The planar zig-zag arrangement could allow the PEO to maximise the interaction with the PMMA segments in the amorphous phase.

In our present study, we examine the miscibility of the blends of stereoregular PMMA and non-ionic surfactants based on oligomers of PEO. This system is interesting from a practical point of view in water based acrylate latex systems, for instance. Actually, after drying, bulk miscibility between acrylate polymer and the surfactant has to be achieved in order to minimised the diffusion of the low molecular weight components toward the interfaces. This diffusion is mainly responsible for the loss in adhesion measured in thin films of paints or adhesives. PMMA/PEO oligomers blends are relevant systems for modelling the miscibility in such industrial formulated films.

The composition range under study is 0–35% of PEO. The influence of the PMMA tacticity, the PEO molecular weight (from 400 to 20,000 g/mol) and the nature of the chain ends (hydroxyl, methyl or butyl) was investigated by DSC and temperature-modulated DSC (MDSC). The single glass transition temperature is the classical criterion of miscibility for our blends. The method developed by Kim and Burns [17–20] was used to determine the interaction parameter in the partially miscible systems by using the experimentally determined T_g.

2. Experimental

2.1. Materials and preparation

The characteristics of the PMMA used in this study are listed in Table 1. The i- and s-PMMA were purchased from polymer source and the a-PMMA was supplied by Aldrich. The characteristics of the PEO based oligomers supplied by Fluka or Aldrich are listed in Table 2. The PEO oligomers are named C_xE_y where x is the number of alkyl groups, C, in the chain and y is the number of ethylene oxide, E, in the chain. For instance, C_1E_{11} corresponds to an oligomer incorporating 11 ethylene oxide groups and one methyl group at the chain end. E_9 is composed of nine EO units and two hydroxyl groups at both ends of the oligomer.

We used five different compositional ratios of the PMMA/PEO blends namely 91/9, 83/17, 77/23, 71/29 and 67/33 (w/w%). The blends were prepared by dissolution of the two polymers in chloroform. The solution was stirred for 24 h and the solvent was evaporated in Petri dishes in a vacuum oven for 24 h at 50°C. The films were cut in small pieces before their introduction into the DSC cups.

Table 1
Characteristics of the PMMA used in this study

PMMA	Tacticity (%) i/h/s	M_n (g/mol)	M_w/M_n	T_g (°C)
iPMMA	97/03/00	37,100	121	60
aPMMA	07/29/64	30,500	1.19	105
sPMMA	00/20/80	30,700	1.05	130

Table 2
Characteristics of the PEO used in this study

PEO	M_n (g/mol)	T_m (°C)	T_g (°C)
E_9	400	7	−72
E_{45}	2000	57	−61
E_{90}	4000	58	−57
E_{454}	20,000	65	−55
C_1E_{11}	550	14	−73
C_4E_3	206	−34	−100

2.2. DSC measurements

The glass transition temperatures were determined using either a Mettler TC11 DSC or a Mettler Star System temperature-modulated DSC (MDSC). For classical DSC measurements, the samples were heated a first time at a heating rate of 10°C/min from room temperature to 150°C. The samples were then rapidly cooled at −150°C at 50°C/min. The second scan was performed at 10°C/min from −150 to 150°C. The temperature modulated DSC (MDSC) measurements were carried out at 1.5°C/min with an oscillating period of 60 s. This technique allows the accurate determination of the T_g of the low content component in a blend and the access to glass transition merged with a melting endotherm, which is often the case of PEO blends with i-PMMA. For the purpose of comparison with MDSC results several traditional DSC measurements were also carried out at 1.5°C/min. During the second scan, the reversing heat flow signal was used to determine the T_g. The experimental error on the determination of the T_g is estimated to be in the range of ±2°C.

3. Results and discussion

3.1. Theoretical background

The approach used to determine χ is based on the shift of the two T_g as compared to the T_g of the pure polymers, due to the phase separation in the blends. The method based on the Flory–Huggins theory [21,22] was modified and applied by Kim and Burns to non-miscible or partially miscible systems such as polystyrene/bisphenol-A caprolactone (PS/PC) [17], PC/polymethyl methacrylate (PC/PMMA) [18], PS/polybutadiene (PS/PB) [19], PC/polyethylene terephtalate [20]. The formalism used in this paper was first developed by Sanchez [23] and slightly modified by Yang and Yetter [24] and Samios [25].

$\chi_{1,2}$ can be deduced for each phase:

$$\tilde{\chi}_{1,2} = \chi_{1,2}/v_r = \frac{\ln(\varphi_1^b/\varphi_1^a) + [1 - (y_1 v_1/y_2 v_2)](\varphi_2^b - \varphi_2^a)}{y_1 v_1[(\varphi_1^a)^2 - (\varphi_1^b)^2]} \tag{1}$$

and

$$\tilde{\chi}_{1,2} = \chi_{1,2}/v_r = \frac{\ln(\varphi_2^b/\varphi_2^a) + [1 - (y_2v_2/y_1v_1)](\varphi_1^b - \varphi_1^a)}{y_2v_2[(\varphi_1^a)^2 - (\varphi_1^b)^2]} \tag{2}$$

The interaction parameter can be calculated according to Eq. (1) or (2) since the composition of the two phases are drawn from the two T_g of the phase separated blend. The interaction parameters calculated will be averaged on the values calculated for the two phases.

The interaction parameter χ_{cr} at the critical point is given by:

$$\tilde{\chi}_c = \chi_{cr}/v_r = \frac{1}{2}\left(\frac{1}{\sqrt{y_1v_1}} + \frac{1}{\sqrt{y_2v_2}}\right)^2 \tag{3}$$

This value χ_{cr} can be the criterion for predicting phase stability: if $\chi < \chi_{cr}$, the blend is in an homogeneous state.

In the case of non-miscible blends, the composition of the separated phases can be calculated from the relations $T_{g_m} = f(w_{i,j}, T_{g_{i,j}})$. Each phase can be considered as a miscible system to which Fox equation [26], Gordon Taylor equation [27] or Couchman equation [28] can be applied. As shown in Fig. 1, the T_g obtained for our blends in the compositional range of 0–40% of PEO fits fairly well with the values obtained from the Fox equation. Therefore, this model will be used in the following treatment of our T_g data

$$\frac{1}{T_{g_m}} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} \tag{4}$$

Eq. (9) is applied to the *a* phase rich in polymer 1:

$$\frac{1}{T_{g_m}^a} = \frac{w_1^a}{T_{g_1}} + \frac{w_2^a}{T_{g_2}} \tag{5}$$

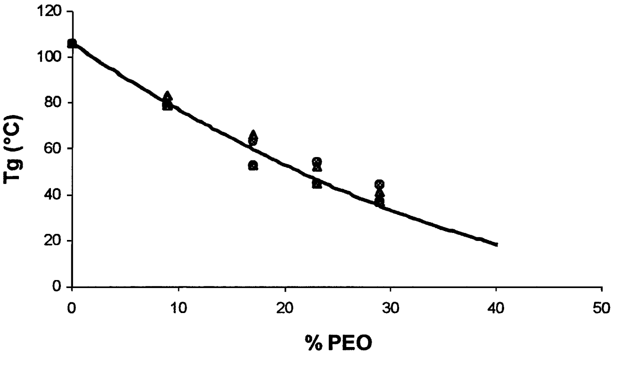

Fig. 1. T_g plotted as a function of the % of PEO for blends of a-PMMA/PEO. The T_g is unique for blends containing less than 20% of PEO and is the T_g of phase rich in PMMA above 20% of PEO. The solid line represents the theoretical T_g values obtained from the Fox law, ■ represents the experimental T_g of a-PMMA/E_9 blends, ▲ represents the experimental T_g of a-PMMA/E_{45} blends and ● represents the experimental T_g of a-PMMA/E_{454} blends.

since $w_2^a = 1 - w_1^a$ the weight fraction can be calculated:

$$w_1^a = \frac{T_{g_1}(T_{g_m}^a = T_{g_2})}{T_{g_m}^a(T_{g_1} - T_{g_2})} \tag{6}$$

where w_1^a, $T_{g_m}^a$, T_{g_1} and T_{g_2} are the weight fraction of polymer 1 in the *a* phase, the T_g of the mixture in the *a* phase and the T_g of the pure polymers 1 and 2, respectively. Once the weight fractions are determined, the volume fractions are calculated from:

$$\varphi_1^a = \frac{\dfrac{w_1^a}{\rho_1}}{\dfrac{w_1^a}{\rho_1} + \dfrac{w_2^a}{\rho_2}}; \qquad \varphi_2^a = 1 - \varphi_1^a \tag{7}$$

where φ_1^a, φ_2^a, ρ_1 and ρ_2 are the volume fractions of polymers 1 and 2 in the *a* phase, respectively, and the densities of polymers 1 and 2, respectively.

4. Results

The DSC thermograms recorded for a-PMMA/PEO blends. Two T_gs are clearly observed for the 23% PEO blends whatever the molecular weight of the PEO. Therefore, it can be concluded that this compositional ratio yields phase separation at a length scale of at least 50 nm. Actually, phase separation occurs between 17 and 23% of PEO for the a-PMMA/PEO blend and the molecular weight of the oligomer does not modify the miscibility window of the mixture. This is consistent with the observations made by other workers [6]. In Fig. 2 the miscibility windows of the different stereoregular PMMA/PEO blends are plotted according to the nature of the PEO oligomer. The compositional range of miscibility is estimated to be 20% of regular PEO, so-called E_9, for a-and s-PMMA and only 10% for i-PMMA in agreement with the results published previously [1–5]. The close behaviour of a- and s-PMMA is explained by the existence in those two stereoisomers of rather long syndiotactic sequences, at least 50%, as shown in Table 1.

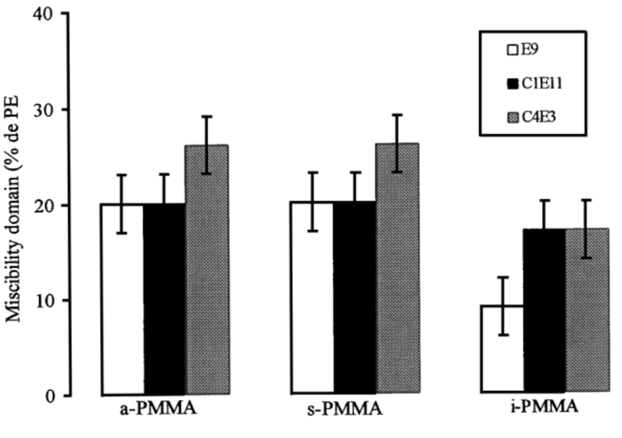

Fig. 2. Miscibility domains determined from the single T_g criterion as a function of the PMMA stereoregularity and the nature of the PEO oligomer.

Table 3

$T_{g17\%}$ is the glass transition temperature of the 17% PEO. $T_{g29\%}^{PMMA}$ and $T_{g29\%}^{PEO}$ are the glass transition temperature of the PMMA and the PEO rich phase, respectively, of the 29% PEO blend. φ_{POE}^{PMMA} and φ_{PMMA}^{POE} are volume fractions of PEO miscible in the PMMA rich phase and of PMMA miscible in the POE rich phase, respectively, from PMMA/POE with 29% of POE by weight. * represents the glass transition temperatures which were determined from MDSC

PMMA	PEO	$Tg_{17\%}$ (°C)	$T_{g29\%}^{PMMA}$ (°C)	$T_{g29\%}^{PEO}$ (°C)	φ_{POE}^{PMMA} (%)	φ_{PMMA}^{POE} (%)
a-PMMA	E_9	53	37	−54	27	17
	E_{45}	62	44	−37	28	19
	E_{454}	65	41	−31	30	22
	C_1E_{11}	54	26	−43	32	26
	C_4E_3	43	24	−63	27	28
s-PMMA	E_9	76	40	−52	29	18
	E_{45}	76	51	−33	28	24
	E_{90}	66	39	−40	34	15
	C_1E_{11}	64	39	−44	31	24
	C_4E_3	58	53	−40	21	41
i-PMMA	E_9	−74 and 7*	20*	−61*	15	18
	C_1E_{11}	15	9*	−55*	22	25
	C_4E_3	28	27		–	–

The particular behaviour of i-PMMA was already reported and ascribed to the specific conformation and high chain stiffness [13] of the isotactic chain segments which weakens the interaction with the PEO chains. Moreover, it should be mentioned that i-PMMA does not crystallise from the melt but only by solvent induction. This means that the i-PMMA/PEO blends are of amorphous/crystalline type. The crystallisation of the PEO chains occurs for lower concentration for the isotactic PMMA isomer than for the other ones. The lower miscibility of i-PMMA as compared to the a- and s-PMMA is observed whatever the molecular weight of the PEO and the nature of the chain ends. Besides, the miscibility domain is generally increased for all the PMMA stereoisomers when the PEO is modified with alkyl chains ends. Indeed, the miscibility window increases from 20% for a- and s-PMMA mixed with E_9 or C_1E_{11} to 25% for blends with C_4E_3. Similarly, the miscibility window for i-PMMA increases from 10% for E_9 to 15% for C_1E_{11} and C_4E_3. The influence of the PEO oligomers chain ends pointed out here stimulated our further investigation in order to understand the origin of this rather unexpected result.

As explained in the theoretical part of this paper, the composition of the two separated phases of a non miscible blend can be drawn from the two determined T_g by using Eqs. (5)–(7). It turns out from the calculated volume fraction of polymer 1 in the phase rich in polymer 2 and reciprocally (φ_{POE}^{PMMA} or φ_{PMMA}^{POE}) that PEO is more miscible in the PMMA rich phase than the inverse as shown in Table 3. Indeed, for the 29% PEO blends φ_{POE}^{PMMA} ranging from 27 to 34% of PEO is incorporated in the PMMA rich phase whereas only 17–22% of PMMA is miscible in the PEO rich phase. This tendency increases with the increase of the PEO molecular weight accordingly with the increase of the PEO crystallinity. Indeed, E_9 oligomer contents 53% of crystalline phase whereas E_{45} and E_{454} polymers are 80% crystalline. Higher crystallisation capacity of the PEO should increase the phase separation if the PMMA chains were totally rejected from the crystalline zone. Actually, Parizel et al. [13] claimed that during crystallisation PMMA chains could be trapped between PEO crystalline lamellae and are, therefore, close to the amorphous PEO chains. Unexpectedly, the proximity of PMMA and PEO chains could be reinforced by higher crystallisation due to higher PEO molecular weight. It is worth noting that these crystalline regions in that low PEO content blends are too small to be detected by DSC and only SAXS measurements can support these assumptions.

Exception to this behaviour is observed for the s-PMMA/C_4E_3 system and for the blends containing i-PMMA for which the fraction of PMMA miscible in the PEO rich phase is higher than the fraction of PEO in the PMMA rich phase. For the blends incorporating i-PMMA the determination of φ_{POE}^{PMMA} is not straightforward since crystallisation occurs and hinders partially the T_g at temperatures close to 10°C. Temperature-modulated DSC is an accurate technique to get insights about the T_g merged with the melting endotherm of the PEO from the reversing part of the signal. From several studies it is admitted that i-PMMA is rejected in the PEO interspherulitic regions [1,13]. This crystalline induced phase separation process allows the growth of spherulites large enough to be detected by DSC that give rise to a third phase of quasi-pure PEO. The PEO content in the two separated amorphous phases is, therefore, weaker which is consistent with what we observed in Table 3.

From the composition of the different phases the $\chi_{1,2}$ interaction parameter can be calculated by using Eqs. (5) and (6) as shown in Table 4. The range of error on the $\chi_{1,2}$ values is estimated to be 4% which is far below the variations observed for the different blends in Table 4. The $\chi_{1,2}$ values averaged over the values calculated for composition of 23 and 29% of PEO in the blends range from 1×10^{-4} to 6×10^{-3}. This is in agreement with the results obtained by Ito et al. [16] from equation of state calculations who claimed that the $\chi_{1,2}$ is close to zero From the Flory–Huggins theory, the interaction parameter can also be

Table 4
Values of the interaction parameters χ_{meas} are measured with the Kim and Burns method and interaction parameters χ_{calc} are calculated from the Van Krevelen tables. The critical interaction parameters χ_{cr} are calculated with the Kim and Burns method. The values of χ_{meas} are averaged over two compositions of the a-PMMA/PEO blends, namely 23 and 29% of PEO by weight

PMMA	PEO	$\chi_{1,2}^{\mathrm{meas}} \times 10^4$	$\chi_{1,2}^{\mathrm{calc}} \times 10^4$	$\chi_{1,2}^{\mathrm{cr}} \times 10^4$
a-PMMA	E_9	32	25	18
	E_{45}	7	6.2	5
	E_{454}	1	4.1	1
	C_1E_{11}	21	5.9	13
	C_4E_3	48	9.7	26
s-PMMA	E_9	30	25	18
	C_1E_{11}	21	5.9	13
	C_4E_3	60	9.7	26
I-PMMA	E_9	39	25	18
	C_1E_{11}	23	5.9	12

expressed as:

$$\chi_{1,2} = (V_r/RT)(\delta_1 - \delta_2)^2 \tag{8}$$

where δ_1 and δ_2 are the Hildebrand solubility parameter for the two components drawn from the Van Krevelen tables [29], V_r the reference volume, R the gas constant and T is the temperature. The most obvious shortcoming of relation (8) is that the interaction parameter can never be negative. The calculated values ranging from 4.1×10^{-4} to 2.5×10^{-3} are also comparable to those obtained from the Kim and Burns methodology. It is worth mentioning that although the values are not strictly equal when comparing the two relations, namely, (1,2) and (8), the same trends are observed. Indeed, the interaction parameter decreases with the increase of the PEO molecular weight as shown in Table 4 since the influence of the hydroxyl end groups relative to the ethyloxy backbone is taken into account in the calculation of the δ_2 Hildebrand parameter. Moreover, comparing the PEO oligomers at roughly identical molecular and different chain end composition, the minimum $\chi_{1,2}$ values is found for the PMMA/C_1E_{11} blend.

It turns out that $\chi_{1,2}$ decreases with the molecular weight of the PEO and that for all the blends $\chi_{1,2} > \chi_{\mathrm{cr}}$ which corresponds to what was expected for phase separated blends. PEO molecular weight has the most significant influence on $\chi_{1,2}$ which decreases from 3×10^{-3} to 1×10^{-4} with an increase of the molecular size. According to the equation of state theory [30,31] $\chi_{1,2}$ is a linear combination of an interactional term and a free-volume term:

$$\frac{\chi_{1,2}}{V_1^*} = \frac{P_1^*}{RT_1^*}\left[\frac{\tilde{V}_1^{1/3}}{\tilde{V}_1^{1/3} - 1}\left(\frac{X_{12}}{P_1^*}\right) + \frac{\tilde{V}_1^{1/3}}{2(4/3 - \tilde{V}_1^{1/3})}\tau^2\right] \tag{9}$$

Interaction free volume

where $\tau = 1 - (T_1^*/T_2^*)$ is the free volume parameter and T_i^*, P_i^* and V_i^* are the characteristic parameters of polymer i. The X_{12} parameter is the contact energy term between polymers 1 and 2 and V_i is the reduced volume of polymer i. The interaction term is generally negative and its increase accounts for a better miscibility of the system whereas the free volume term is positive and gives an unfavourable contribution to the miscibility. The first term of the formula depends only on the interaction between the components of the blend and is, therefore, independent of the molecular weight of the PEO. In contrast, the free volume term is strongly molecular weight dependent especially when one of the component is in the liquid state and the other one in the solid state at a given temperature. Indeed, the free volume parameter τ is larger for polymer-solvent systems than for polymer-polymer blends, namely, in the order of 0.4 and 0.15, respectively [30]. Since E_9 is in the liquid state at room temperature the blend with a-PMMA is, therefore, expected to exhibit a higher $\chi_{1,2}$ than E_{45} or E_{454} which are solid polymers.

The $\chi_{1,2}$ values are not found strongly tacticity dependent for the two alkyl chain end modified PEO oligomers but stereoregularity is slightly more significant for hydroxyl terminated PEO. For instance, the interaction parameters are ranging from 20×10^{-4} to 23×10^{-4} for the PMMA/C_1E_{11} blend but from 30 to 39×10^{-4} for E_9. A higher tacticity dependence of the interaction parameter was expected by considering that on the one hand the entropic contribution to the interaction parameter is important in this system [16] and on the other hand that significant differences exist in the chain stiffness between PMMA stereoisomers [32]. Moreover, Vorenkamp et al. [33] have reported characteristic temperatures T^* at 393 K of 7788 and 8075 K for i- and a-PMMA, respectively. This should account for differences in the free volume contribution to the interaction parameter between the two PMMA stereoisomers. However, it is worth noting that the influence of PEO cristallinity superimposes to the interaction of PEO/PMMA molecules in the amorphous phase. Therefore, we can assume that the development of the crystalline phase at low PEO content for i-PMMA/PEO blends is the main difference arising from PMMA stereoregularity. Consequently, the interaction parameter calculated from the T_g of the two separated phases in the amorphous state are found rather independent of the PMMA tacticity.

Table 4 shows the values of χ and χ_{cr} for the different stereoregular PMMA blended with PEO with different nature of chain ends. In each cases $\chi \geq \chi_{\mathrm{cr}}$ which means that the system is phase separated at concentrations between 23 and 29% of PEO. This is confirmed by the two T_g observed for these systems on the DSC thermograms. One of the main interesting feature of that blends of PMMA with PEO oligomers is that $\chi_{C_1E_{11}/\mathrm{PMMA}} \leq \chi_{C_4E_3/\mathrm{PMMA}}$. At a molecular level, replacing an hydroxyl group by a methyl group at the end of the PEO chain is not expected to enhance the interactions with PMMA. In contrary, dipole–dipole or H-bonds would have been envisaged to take place between one –OH chain end of PEO and a carbonyl group of PMMA side-chain. Therefore, the interaction contribution to the $\chi_{1,2}$ is not supposed to be prevalent in this blend. It should also be noticed that slightly different number of ethylene oxide (EO) segments are present in the different oligomers. A tentative correlation can be made between the number of EO segments in the oligomer and the $\chi_{1,2}$. All the points are well fitted by a power law relation written as $\chi_{1,2} = \mathrm{EO}^{-4/5}$. No deviation due to the nature of the chain ends is observed. In conclusion, the entropic contribution to the interaction parameter through the free volume term of relation (9) is likely to be dominant but only depends on the size of the EO sequences in the PEO chain and is independent of the chemical nature of the chain ends. More questioning is the fate of the apolar alkyl chains ends in such blends reported as miscible at a molecular level [1]. Actually, there are also papers indicating that some phase separation in the amorphous phase may occur at low PEO concentrations [34]. We could, therefore, assume the existence of restricted size separated domains embedding mainly PEO chain ends either in the intraspherulitic or in the interspherulitic regions for low molecular weight polymers.

Although the PMMA/C_4E_3 blends provide relatively high values of the interaction parameter, namely, 49×10^{-4} and 60×10^{-4} for the a- and s-PMMA, respectively, only a single T_g is observed for that blends even at 23% of PEO. It should be remembered that at that PEO content all the other blends exhibit two T_gs. From these observations, it should be noticed that the unfavourable contribution of the free volume to the interaction parameter is not the only factor affecting the miscibility. Hence, the negative combinatorial entropy that is a significant factor in determining the sign of the free energy since the mixing enthalpy is positive, increases with the decrease of the molecular weight of the polymers. Therefore, there can be a balance between the unfavourable contribution of low polymerisation degrees to the $\chi_{1,2}$ and the gain in entropy which ensues which provides stable values of the free energy of mixing. Indeed, the free energy of mixing, calculated from the Flory–Huggins theory, ranges from -7.5×10^{-5} to -20×10^{-5} J for E_9 and E_{45}, respectively. This is in agreement with the observation of similar compositional miscibility domains whatever the molecular weight of the PEO for a given stereoregularity of the PMMA. The point of the chain ends effects on the miscibility domain is less straightforward to understand. Actually, one of the assumption is that the very low molecular weight of the C_4E_3, as compared to the other oligomers, is sufficient to strongly increase the combinatorial entropy and, therefore, leads to negative values of the free energy of mixing. The second hypothesis is based on the PEO crystallisation induced phase separation suggesting that PMMA is present in interfibrillar or interlamellar zones of PEO crystal. The thermograms obtained after quenching the samples of pure PEO oligomers at 50°C/min at −150°C are plotted in Fig. 3. It turns out that E_9 and C_1E_{11} oligomers only exhibit a melting endotherm whereas C_4E_3 presents an additional large crystallisation exotherm and a clearly observable T_g due to its amorphous state at −150°C. It can be concluded that during cooling crystallisation occurs in the E_9 and C_1E_{11} samples whereas it is hindered at that cooling rate in the C_4E_3. This rate which is the highest available for our DSC apparatus is too slow to lead to a real quenching process for the E_9 and C_1E_{11} oligomers. In contrary, crystallisation is hindered for the C_4E_3 oligomer since kinetics of chain mutual arrangement in crystallites is likely to be lowered by the presence of large butyl chain ends and the few EO units. In the PMMA/C_4E_3 blends crystallisation is probably not the relevant phenomenon inducing phase separation which proceeds, therefore, at higher PEO contents. This last point will motivate further inquiries on these systems using more sophisticated techniques such as solid-state NMR, WAXS or neutron scattering.

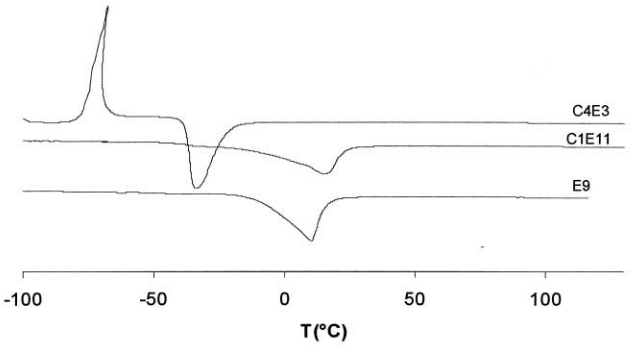

Fig. 3. DSC thermograms of the pure PEO oligomers during the second scan. Crystallisation exotherm is only observed for C_4E_3.

5. Conclusions

The miscibility of PMMA/PEO oligomers blends was studied from the glass transition temperatures which allows the determination of the miscibility domains, the composition of the separated phases and the interaction parameters. The influence of three factors was investigated and the main conclusions can be summarised as follows: The molecular weight of PEO plays a major role on the phase composition. The PEO and PMMA chains content increases in the PMMA and PEO rich phases, respectively, when the PEO molecular weight increases. This is correlated with a decrease of the interaction parameter because of the lowering of the free volume contribution.

The PMMA syndiotacticity increases the miscibility domain but does not modify the interaction parameter in the amorphous phase. Crystallinity is found to be the major factor influencing the miscibility according to the PMMA stereoregularity.

PEO chain ends influence both the miscibility domain and the interaction parameter. Lower $\chi_{1,2}$ is obtained for the methyl modified PEO and larger miscibility domains are determined for the butyl terminated PEO. Crystallisation kinetics seem to be responsible for this last effect.

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