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# THERMAL BEHAVIOUR OF POLYMER BLENDS CONTAINING POLY(MONO-ITACONATES) AND POLY(THIOCARBONATES)

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## ABSTRACT

Six polymer blends of poly(mono-itaconates) with poly(thiocarbonates), both with different side chains, have been studied by DSC measurements. The variation of the glass transition temperature ($T_g$) as a function of the composition of the mixture has been investigated for different mixtures. Blends of poly(thiocarbonates) with poly(monomethyl itaconate) seem to be miscible over the whole range of compositions. All blends show only a single value for the glass transition temperature, intermediate between those of the poly(thiocarbonate) and the decomposition temperature of the poly(itaconate). These results suggest that these blends are miscible for every composition investigated. Blends containing poly(monoethyl itaconate) seem to give rise to a polymer–polymer complex. The $k$ parameter of the Gordon–Taylor equation obtained for the former blends is 0.43, 0.48 and 0.51, for blends containing poly(thiocarbonates) with methyl, ethyl and propyl groups as the side chain, respectively.

## INTRODUCTION

The glass transition temperatures ($T_g$) of polymer mixtures are important in the study of polymer compatibility [1–6]: compatible polymer blends exhibit a single $T_g$ value intermediate between the $T_g$ of the individual components, whereas incompatible blends show two $T_g$ values at a given composition, indicative of phase separation. In general, it is observed that $T_g$ increases monotonically as a function of composition, with a more or less pronounced negative deviation from linearity [7]. Several theoretical equations have been proposed to explain the $T_g$–composition dependence of miscible polymer blends. These equations have been derived from the so-called free volume hypothesis or from thermodynamic arguments, assuming the continuity of the entropy of the mixture at $T_g$ [7].

The miscibility between two polymers is often due to the complementary dissimilarity of their structures, giving rise to specific interactions between

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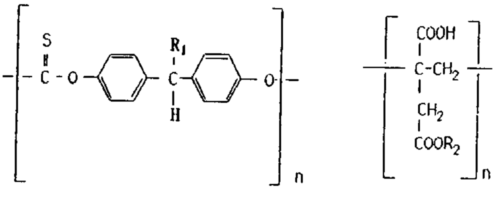
their repeat units. One of the conditions for miscibility is that these specific interactions, often acid–base interactions, have to be stronger than the dispersive van der Waals forces which oppose miscibility. Normally the mixing of two polymers is enthalpically controlled since the entropy contribution is vanishingly small for high molecular weight polymers. Therefore, in order to ensure that a single-phase blend is obtained, the heat of mixing must be negative or at least not significantly positive. For the majority of polymer combinations, the component repeat units are sufficiently different that the heats of mixing, which reflect the contact interactions between dissimilar components, will be unfavourable and a two-phase system will be the usual result. To ensure miscibility, it is therefore necessary to match carefully the polymer repeat units or to ensure that some favourable specific interactions can exist between the chains. The later condition can be achieved in a number of ways [1], for example through favourable dipole–dipole or donor–acceptor interactions, or by incorporating acid and base functions [8].

There are several works dealing with the thermal behaviour of polymer mixtures containing poly(carbonates) [9–11] because of the industrial interest in this kind of polymers. Poly(thiocarbonates) (PTC) form a family of polymers closely related to poly(carbonates), having rather similar properties with respect to their solution behaviour [12–15].

The aim of this work is the study of the thermal behaviour of polymer mixtures containing poly(thiocarbonates) and poly(mono-itaconates) (PMI) with different side chain structures (See scheme 1). Poly(thiocarbonates) have an–OCS–group which can interact specifically with the –COOH group of poly(mono-itaconate) giving rise to a compatible polymer mixture. The glass transition temperatures of poly(thiocarbonates) have been well studied,



**Poly(thiocarbonate)** **Poly(monoitaconate)**

| | | | |
|---|---|---|---|
| $R_1$ - $-CH_3$ | (PHMTC) | $R_2$ - $-CH_3$ | (PMMI) |
| $R_1$ - $-CH_2$-$CH_3$ | (PHETC) | $R_2$ - $-CH_2$-$CH_3$ | (PMEI) |
| $R_1$ - $-(CH_2)_2$-$CH_3$ | (PHPTC) | | |

Scheme 1.

but poly(mono-itaconates) with small substituents do not show a clear glass transition temperature. Nevertheless, it should be interesting to study the mixtures of these polymers because they represent an interesting polymer blend from the thermal point of view.

## EXPERIMENTAL

### *Monomer and polymer preparations*

The poly(thiocarbonates) were synthesised by phase transfer catalysis, as previously reported [16,17].

Mono-methyl itaconate (4-methyl hydrogen-2-methylene succinate) and mono-ethyl itaconate (4-ethyl hydrogen-2-methylene succinate) were prepared by reaction of itaconic acid (2-methylenesuccinic acid) with the corresponding alcohol under fairly acidic conditions, according to the method described by Baker et al. [18] for lower monoesters. Purification was achieved by repeated dissolution in methanol and precipitation in diethylether. Monomers were polymerised at 343 K in bulk under $N_2$ and in the presence of 2,2′-azobisisobutyronitrile (AIBN) (0.25 mol%) as initiator; the polymer yield was 55%.

### *Molecular weight determination*

The weight average molecular weight $M_W$ of the polymers and the polydispersity indices of the polymer fractions were determined by size exclusion chromatography (SEC) using a Perkin–Elmer high performance liquid chromatograph (HPLC) equipped with a 6000 psi pump, a Perkin–Elmer differential refractometer model LC-25 and an injector volume of 175 μl. Three Water Associate Ultra Styragel™ columns ($10^3$, $10^4$ and $10^5$ Å) were used in series. Tetrahydrofuran was used as eluent and the flow rate was 1 ml $\text{min}^{-1}$. The columns were first calibrated with standard polystyrene samples of narrow molecular weight distribution. A calibration curve of the type $\log M = f(V_e)$ was used, where $V_e$ is the peak elution volumes for polystyrene standards. The $M_W$ and $M_n$ values of the polymers were calculated with the aid of a computer program based on normalisation of the chromatograms [19].

### *Preparation of the blends*

The blends were prepared by means of solution casting, using dioxane as solvent. The polymer concentration in the solution was about 5%. Dioxane evaporation was conducted at room temperature. The resulting films were dried in a vacuum oven at 50 °C over 72 h.

### *Differential scanning calorimetry (DSC)*

The glass transition temperatures ($T_g$) of the polymers and mixtures were measured using a Mettler TA-3000 calorimetric system equipped with a TA-processor and a DSC-20 cell. Polymer samples were dried under reduced pressure in a vacuum oven prior to measurements. Samples (10–15 mg) were weighed into the DSC aluminium pans. Dry nitrogen was used as purge gas and thermograms were measured between 300 and 500 K at a scan rate of 10 K min$^{-1}$. Regular calibration of the instrument was carried out using metal standards.

Before measuring the glass transition, all samples were first heated to the upper temperature limit (400 K) and quenched to the starting temperature in order to minimise differences in the thermal history. The glass transition was indicated by baseline shift on the thermogram and $T_g$ was estimated from the point of intersection of the sloping portion of the curve resulting from the baseline shift.

## RESULTS AND DISCUSSION

The glass transition temperatures ($T_g$) of poly(thiocarbonates) were 372, 367 and 403 K for PHMTC, PHETC and PHPTC, respectively. In contrast, the thermograms for poly(mono-itaconates) are relatively featureless between 100 and 400 K and it is very difficult to identify positively the transition. At temperatures higher than 400 K, it seems that some decomposition of the poly(itaconate) takes place. A similar behaviour for low poly(mono-itaconates) has been reported by Cowie and Haq [20]. In general, it is difficult to obtain clear $T_g$ values for poly(mono-itaconates), although some relaxations related with the $T_g$ have been reported for poly(mono-itaconates) [20,21]. Nevertheless, we have recently reported the glass transi-

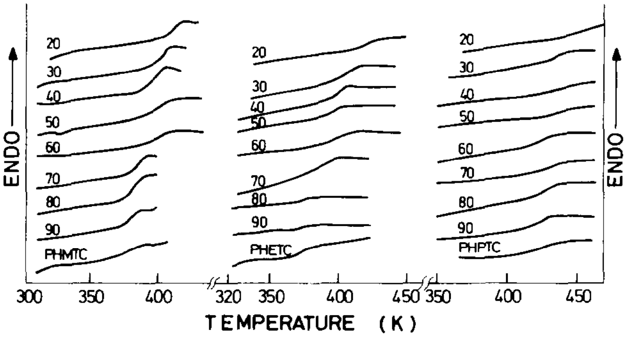


Fig. 1. Thermograms for blends containing PHMTC, PHETC and PHPT with PMMI, at different compositions.

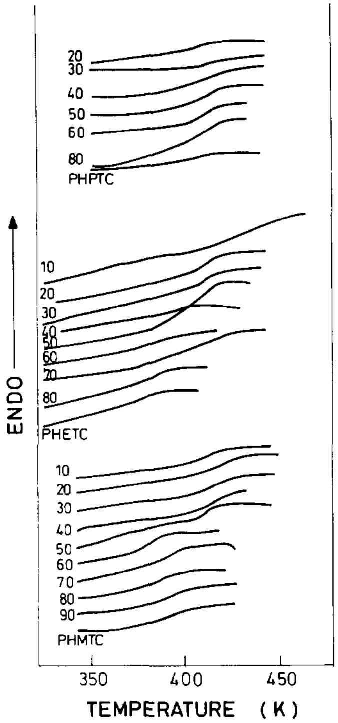


Fig. 2. Thermograms for blends containing PHMTC, PHETC and PHPT with PMEI, at different compositions.

tion temperature for poly(monobenzyl itaconate) determined by calorimetry, a value which is very close to that of the $\alpha$-relaxation previously reported [21,22].

Figures 1 and 2 show the most representative DSC thermograms in the $T_g$ region for mixtures of different compositions of PTC containing PMMI and PMEI, respectively. As the figures show, there is distinct evidence of only a single glass transition for each of the different blend compositions, intermediate between the glass transition of poly(thiocarbonate) and the decomposition temperature of poly(itaconate). When the blend contains PMMI, there is a continuous variation in the $T_g$ value (Fig. 3), while in the case of those blends containing PMEI, a sigmoidal behaviour is observed which suggests a strong tendency towards a common composition, irrespective of the starting composition (Fig. 4). Table 1 summarises the $T_g$ values for blends of PTC with PMMI and PMEI, respectively, and the different compositions of the blends.

Figure 3 shows that blends containing PMMI have a monotonic variation of $T_g$ with composition. This variation depends on the side chain structure of poly(thiocarbonate). As can be seen, the differences between the curves dealing with the variation of $T_g$ with composition of the blends and the

TABLE 1

Glass transition temperature, $T_g$ (K), for blends of PHMTC, PHETC and PHPTC with PMMI and PMEI

| | PHMTC | PHETC | PHPTC |
|---|---|---|---|
| PMMI (wt.%) | | | |
| 0 | 372 | 367 | 403 |
| 10 | 373 | 369 | 404 |
| 20 | 378 | 372 | 405 |
| 30 | 383 | 376 | 406 |
| 40 | 387 | 383 | 406 |
| 50 | 395 | 387 | 407 |
| 60 | 401 | 394 | 409 |
| 70 | 407 | 401 | 412 |
| 80 | 416 | 410 | 415 |
| 100 | 432 [a] | 432 [a] | 432 [a] |
| PMEI (wt.%) | | | |
| 0 | 372 | 367 | – |
| 10 | 372 | – | 403 |
| 20 | 373 | 368 | 403 |
| 30 | 374 | 370 | – |
| 40 | 375 | 370 | 403 |
| 50 | 398 | 385 | 404 |
| 60 | 400 | 397 | 404 |
| 70 | 400 | 398 | 406 |
| 80 | 402 | 400 | 408 |
| 90 | 405 | 403 | – |
| 100 | 135 [a] | 135 [a] | 135 [a] |

[a] Estimated by extrapolation from Figs. 3 and 4.

mean value between the $T_g$ of the pure components are quite different depending on the side chain structure of the poly(thiocarbonate). It is necessary to note that the $T_g$ value of PMMI represented in Fig. 3 is the $T_g$ value obtained by extrapolation of the $T_g$ values of the blends to that of the pure component, and also that this $T_g$ value corresponds to the temperature at which the thermograms indicate an apparent decomposition. The apparent $T_g$ value for PMMI considered in this work is in good agreement with the endotherms reported by Cowie and Haq [20] for low poly(mono-itaconates) and with the α-relaxation reported by the same authors [20]. Therefore although the apparent $T_g$ value reported for PMMI in this work could be uncertain, the shape of the variation of the $T_g$ of mixtures with composition could be considered to approximate the real $T_g$ value of PMMI. The experimental $T_g$ value of PMMI has not been obtained, but in accordance with our calorimetric results of mixtures containing PMMI, it is possible to assume that the $T_g$ value of this polymer is around 160 °C.

In the case of blends containing poly(monoethyl itaconate) (see Fig. 4) there is no significative variation of $T_g$ with composition in the range 0 to

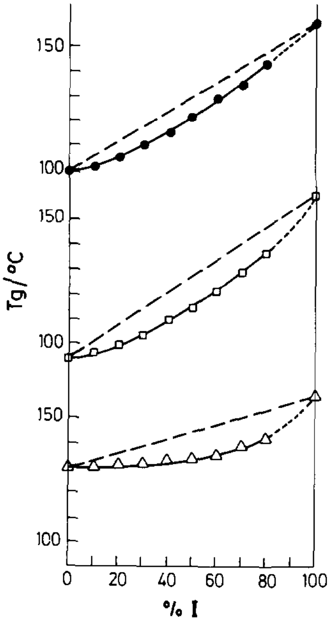


Fig. 3. Variation of the glass transition temperature ($T_g$) with composition (%$I$) for blends of PMMI with PHTMC (●), PHETC (□) and PHPTC (△).

≈ 50% depending on the blend, but a sharp discontinuity is observed at about 50% composition when the $T_g$ value remains approximately constant up to the decomposition temperature of PMEI. This behaviour could be attributed to a probable polymer–polymer complex formation between the

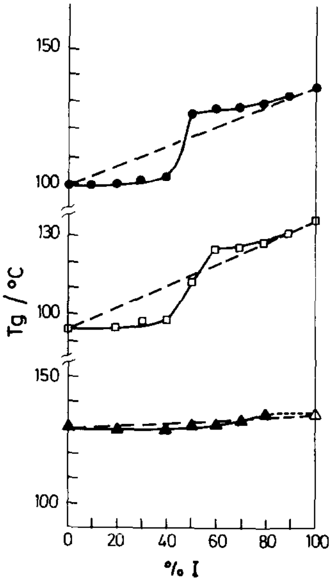


Fig. 4. Variation of the glass transition temperature ($T_g$) with composition (%$I$) for blends of PMEI with PHMTC (●), PHETC (□) and PHPTC (▲).

components of the blend, where the stoichiometry of the complex should be 1 : 1. A similar result has been reported by Cowie et al. [23] for the mixture poly(acrylic acid)–poly(vinyl methyl ether).

Therefore, according to these results it could be possible to assume compatibility between poly(thiocarbonates) and poly(monomethyl itaconate) while in the case of the blends containing PMEI, polycomplex formation is presumed to occur at ≈ 50% composition. In the former blends, an extensive mixing of the segments of the two polymers may be assumed. In order to represent the $T_g$–composition variation, we have applied the Gordon–Taylor [24] treatment for the $T_g$ of polymer blends, using the equation

$$T_g = (w_1 T_{g1} + k w_2 T_{g2})/(w_1 + k w_2) \tag{1}$$

where $T_g$ is the glass transition temperature of the blend and $T_{g1}$ and $T_{g2}$ are those of components 1 and 2, $w_1$ and $w_2$ are the corresponding weight fractions, and $k$ is an adjusting parameter related to the degree of curvature of the $T_g$–composition plot. The $k$ value obtained for our experimental results are 0.43, 0.48 and 0.51 for blends of PHMT, PHET and PHPT with PMMI, respectively. The $k$ parameter of the Gordon–Taylor equation can be taken as a taken as a semiquantitative measure of the strength of the interaction between the components of the blends, as Belorgey and Prud'homme have pointed out [25]. In fact, in the $T_g$–composition plots a concavity is observed even in polymer–polymer blends which present strong interactions [2,26–29]. According to experimental results previously reported for different kinds of polymers, this concavity can be considered as inversely proportional to the strength of the interaction between the two polymers in the mixture [25]. Therefore it is possible to conclude that the strength of the interaction in blends of PTC with PMMI decreases as the size of the side chain of PTC increases.

## CONCLUSIONS

We can conclude that the variation in the $T_g$ of blends containing poly(mono-itaconates) can be used to estimate the approximate $T_g$ of the poly(mono-itaconate). Blends of PTC with PMMI and PMEI show a different behaviour: those containing PMMI seem to be miscible and the strength of the interaction depends on the structure of the side chain in the PTC; but those containing PMEI apparently give rise to a polymer–polymer complex with a well defined stoichiometry.

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