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Semi-Rigid Polyesters Analysed Using the "Strong-Fragile" Concept

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SUMMARY: Semi-rigid polyesters from diphenyl dicarbonic acid and some branched propyl and butyl spacers have been investigated using Differential Scanning Calorimetry. From Δc_p at Tg and the determination of the fragility index m, we studied the "strong-fragile" behaviour of these materials. All the samples appear thermodynamically "strong" and "kinetically" fragile. A comparison of these results with those obtained from glass-forming liquids leading to linear polymers - such as PET, PCT, PEN or poly-methyl (α-n-alkyl) acrylates- shows that a modification of the polymer rigidity leads to change the fragility index m and the Δc_p at the glass transition.

Introduction:

Structural relaxation is a general phenomenon, that occurs when a glass is maintained at a temperature Ta below its glass transition temperature Tg. This is generally called physical ageing [1]. Consequently, ageing implies the variation with time of many glass properties, such as the enthalpy variations presented in Figure 1.

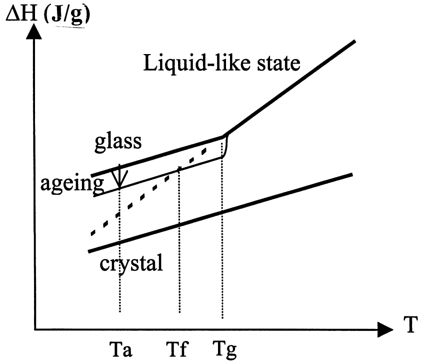

Figure 1. enthalpic variations during structural relaxation (or physical ageing).

The liquid-glass transition is experimentally characterised by the glass transition temperature Tg, often defined either as the temperature at which the equilibrium liquid has a viscosity

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equal to 10^{13} Pa.s [2], or as the temperature at which the average relaxation time in the equilibrium liquid is equal to 100s. From some data concerning solutions and polymers, Angell [2] has observed that the variations of the viscosity with the temperature, and more exactly with the normalised reduced quantity T_g/T, are included between two limits. An Arrhenius law describes the first limit, leading to the so-called "strong" glass-forming liquid behaviour, while a Vogel-Tamman-Fulcher law describes the second, leading to the "fragile" glass-forming liquid behaviour (Figure 2). Because all glass-forming liquids are located between these two limits, a classification was been proposed by Ngai e. a.[3] using the fragility index m defined as:

$$m = \left.\frac{d\log_{10}(\tau)}{d\left(\frac{Tg}{T}\right)}\right|_{T=Tg} \qquad (1)$$

Where τ is the relaxation time [s], T is the actual temperature and Tg is the glass transition temperature [K]. The two limits are reached for m = 16 ("strong" glass-forming liquid) and m ≥ 200 ("fragile" glass-forming liquid) [4].

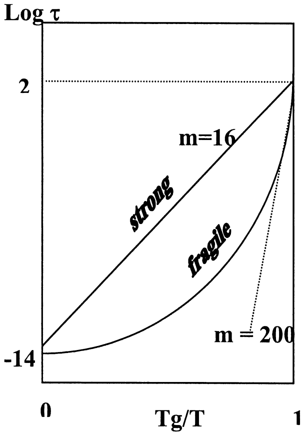


Figure 2. Dependence of the average relaxation time on the Tg-scaled reciprocal reduced temperature.

According to the Gibbs theory [5], it is possible to associate the average height of the energy barrier which relaxing entities have to pass to reach their minima energy to the value of m. However, it has also to be taken into account that the number of minima available for the relaxation differs from material to material. This number is proportional to $\Delta c_p = [c_{pl}-c_{pg}]_{T=Tg}$, (difference between the values of the heat capacity in the liquid and in the glassy state at the glass transition temperature) [6,7]. Thus, the value of the fragility index m characterises in fact a kinetic aspect, while the Δc_p value characterises a thermodynamic aspect. When the variations of the specific heat at the glass transition are low (Δc_p = 0.15 J/K.g) this indicates that the accessible energy minima density is small and the glass-forming liquid is thermodynamically "strong" (TS). However, if this density is high, the glass-forming liquid will be thermodynamically "fragile" (TF: large variation of the specific heat at the glass transition, Δc_p = 0.35 J/K.g). From the kinetic point of view, if the value of m is low, this can be interpreted as a high average potential energy barrier between the different possible minima and the corresponding glass-forming liquid is called kinetically "strong" (KS), whereas for a high value of m, we will have a kinetically "fragile" glass-forming liquid (KF). To sum up, the "strong-fragile" concept delivers four extreme possibilities (see Figure 3) by combination of thermodynamic and kinetic aspects [7], so that any glass-forming liquid can be characterised as (TS-KS), (TF-KF), (TF-KS), or (TS-KF).

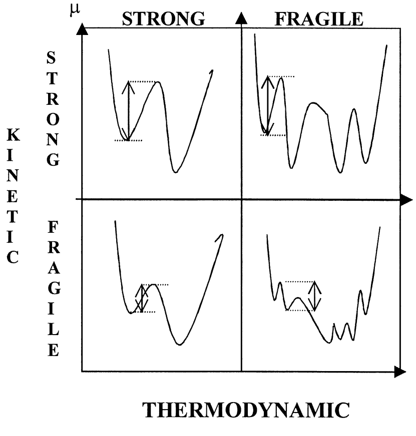


Figure 3. Schematic representation of the potential energy μ versus the configuration space.

Thermodynamic Aspect

kinetic aspect	**TS,KS** GeO_2 [8] $Se_{92}Ge_8$ [9] $Se_{88}Ge_{12}$ [9]	**TF,KS** C_5, C_8 [11]
	TS,KF $Ge_{15}Te_{85}$ [10] Se [9]	**TF,KF** Epoxy [12] PET, PEN, PCT [13] C_1, C_3 [11]

Figure 4. Illustration of this schematic representation with data collected in the literature.

A review of data collected from the literature [8-13], interpreted with the "strong-fragile" concept, shows that the majority of glass-forming liquids leading to linear polymers can be classified as thermodynamically "fragile" and kinetically "fragile" (TF-KS), see Figure 4. In this work, we have studied some linear semi-rigid polymers and we compare the results with those obtained for others linear polymers using the theoretical concept outlined above.

Model and Method:

Experimentally, the heat capacity variations at the glass transition are very easy to determine by using e. g.: differential scanning calorimetry. The calculation of m requires a mathematical expression for the relaxation time. For a glass, the Tool-Narayanaswamy-Moynihan (TNM) expression is often used [14,15,16]:

$$\tau = \tau_0 \exp\left(\frac{x\Delta h^*}{RT}\right)\exp\left(\frac{(1-x)\Delta h^*}{RT_f}\right) \tag{2}$$

where x ($0<x<1$) is the non-linearity parameter or Narayanaswamy parameter, Δh^* the apparent activation energy and T_f is the fictive temperature [14]. Introducing formula (2) in (1), and when experiments are carried out starting from the liquid state ($x=1$), the following relation for m is obtained:

$$m = \frac{\Delta h^*}{R\overline{T_f}\ln(10)} \tag{3}$$

Experimentally, the value of Δh^* can be determined from the variations of the fictive temperature with the cooling rate according to the relationship proposed by Moynihan [16]:

$$\frac{d\ln(|q^-|)}{d(1/T_f)} = \frac{-\Delta h^*}{R} \tag{4}$$

The fictive temperature, characteristic of the structure of the material, depends on the cooling rate q^- applied to the material and can be calculated graphically using the so called 'equal areas' construction [16].

Thus, it is possible to investigate all the aspects (kinetic and thermodynamic) defined in the "strong fragile" concept calorimetrically.

Experimental:

The semi-rigid polymers studied in this work were synthesised in the Physical Chemistry laboratory of Duisburg by M.Hess e. a. (see Figure 5).

The polyesters poly[oxy(2,2 dialkylpropane - 1,3 - diyl)carboxylbisphenyl - 4,4' dicarbonyl] are abbreviated DP1.1, DP1.2 and DP1.3 respectively. The numbers indicate the number of carbons of the side chain attached to the tertiary carbon of the propyl spacer. The molar masses of the polymers were determined with size exclusion chromatography in line with multi angle laser light scattering. The average molar masses, <Mw> (mass average) and <Mn> (average number) are given in Table 1.

Table 1. Values of <Mw> and <Mn> for each sample.

Polymer	**<Mw>/g.mol^{-1}**	**<Mn>/g.mol^{-1}**
DP1.1	13 700	5 200
DP1.2	27 000	9 400
DP1.3	36 500	7 200

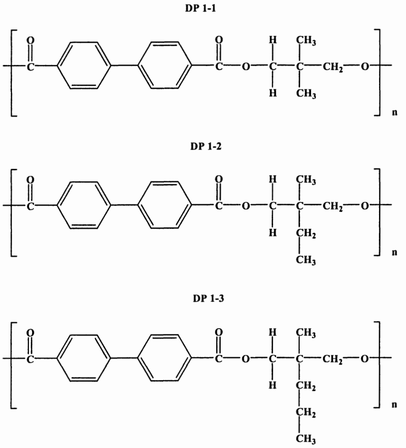


Figure 5: Chemical formula of DP1.1, DP1.2 and DP1.3 samples.

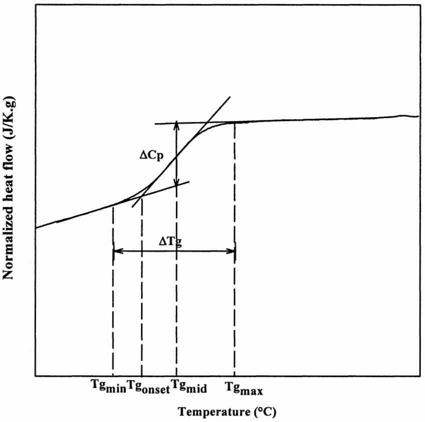


Figure 6: Definition of the measured Δc_p and ΔTg.

These polymers show a clear glass transition and weak, sometimes monotropic first order transitions at higher temperatures, which indicate melting and probable mesophase transitions [17]. In this work, only the glass transition is studied. Differential scanning calorimetry (DSC) was performed with a Perkin Elmer Series 7 calorimeter. Experiments were carried out under a nitrogen flow at a heating rate of 20°C/min. The calorimeter was calibrated with regard to temperature and energy with Indium and Zinc. ΔTg and Δc_p values for each DSC curve were determined as shown in Figure 6. Finally, the same sample was used for all thermal cycles to limit the statistical data scattering.

Results and Discussion:

Figure 7-9 show the DSC curves obtained during the heating period for DP1.i samples previously cooled at the indicated cooling rate q^-. The fictive temperature Tf was evaluated for each curve and the linear dependence of reciprocal Tf with ln (q^-) is shown in figure (10). The slope of each curve allows us to estimate the value of the apparent activation energy Δh^* for each sample. In Table 2, we have reported the values of the specific heat step Δc_p at the glass transition, the glass transition domain ΔTg, the apparent activation energy Δh^* and the fragility index m for the three different samples.

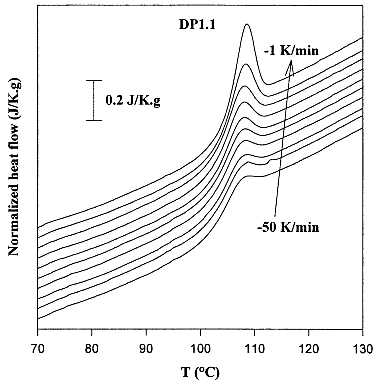


Figure 7. DP1.1: DSC curves obtained for various cooling rates.

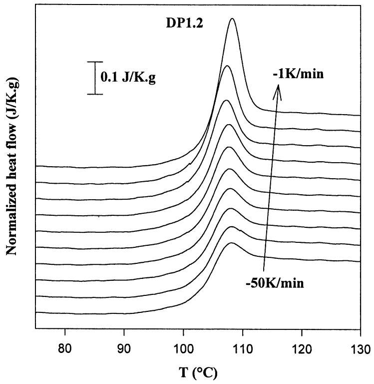


Figure 8. DP1.2: DSC curves obtained for various cooling rates.

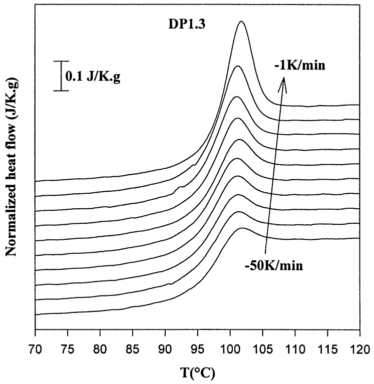


Figure 9. DP1.3: DSC curves obtained for various cooling rates.

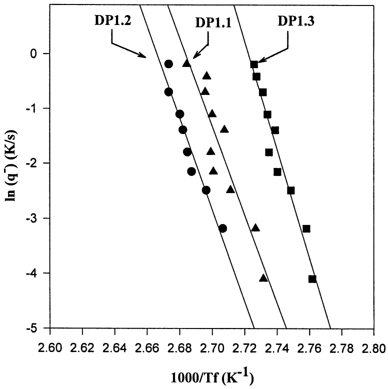


Figure 10. Determination of Δh^*:
DP1.1 - 671 kJ/mol;
DP1.2 - 698 kJ/mol;
DP1.3 – 823 kJ/mol

Table 2. Comparison of the structural relaxation parameters between DP1.i samples and other linear polymers. In this work, Tg_{mid} is determined for $q^{+}=q^{-}=20K/min$.

Sample	Tg (°C)	ΔTg (°C)	Δc_p (J/K.g)	Δh* (kJ/mol)	m	reference
DP1.1	102.2 (mid)	21.8 ± 0.8	0.20 ± 0.01	671	93	This work
DP1.2	99.2 (mid)	20.8 ± 0.8	0.20 ± 0.02	698	98	This work
DP1.3	94.8 (mid)	23.4 ± 1.5	0.21 ± 0.01	823	117	This work
PET	75 (onset)	15	0.31	1106	166	13
PEN	120 (onset)	20	0.27	1089	145	13
PCT	87 (onset)	18	0.24	890	129	13
C1	115 (onset)	30	0.27	998	120	11
C3	63 (onset)	32	0.33	865	135	11

Furthermore, we have determined the values of the parameters Δc_p and m, characterising the thermodynamic and the kinetic aspects of Angell's "strong-fragile" concept, respectively. For the three DP1 samples, we conclude that they are kinetically "fragile", the m values being 93, 98 and 117 for DP1.1, DP1.2 and DP1.3 respectively. Concerning the thermodynamic aspect, we cannot immediately conclude. Indeed, the Δc_p value found of about 0.20 J/K.g, which is in the middle of the expected Δc_p variation range. We can, however, compare these results with those obtained for some glass-forming liquids leading also to linear polymer structures, such as PCT, PEN and PET by plotting the data couples (Δc_p,m) as shown displayed in Figure 11.

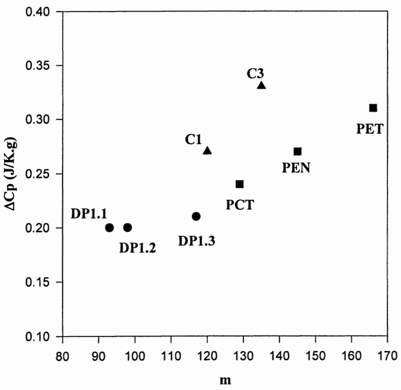


Figure 11. Comparison of the ΔCp/m couples for different glass-forming liquids leading to linear polymers.

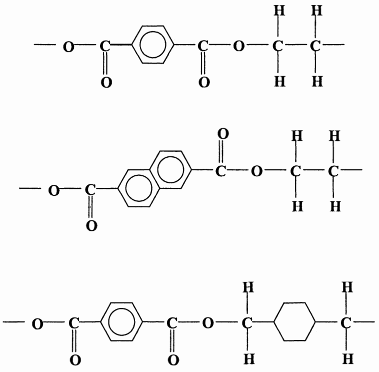
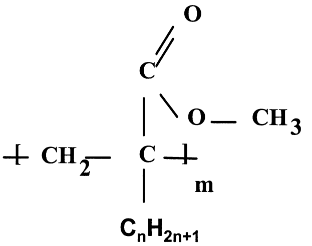


Figure 12: chemical formula of PET, PEN and PCT from up to down.

Thus, we may say that the DP1 samples are thermodynamically and kinetically "stronger" than PET, PCT and PEN. If we compare the chemical structure of these linear polymers (see Figure 12), we observe that increasing rigidity of the main chain (induced by the aromatic systems) leads to "stronger" and "stronger" glass-forming liquids. This result leads us to the conclusion that when the flexibility of the main chain decreases, the kinetic and thermodynamic behaviour grows "stronger".

A second comparison can be performed now with data obtained from the poly-methyl (α-n-alkyl) acrylate family (Figure 13). We have studied the influence of the length of the lateral chain. When we compare the variations of m between these two types of polymer (the flexible-chain acrylates and the more rigid aromatic branched esters), and in particular when we do so for the same lateral chain length variations (C1, C3) and (DP1.1, DP1.2, DP1.3), we find that the fragility index increases for a carbon number varying from 1 to 3 in both cases. When we compare the thermodynamic behaviour, the DP1 samples are "stronger" than the poly-methyl (α-n-alkyl) acrylate samples. This is due to the greater rigidity of the polymer skeleton of the linear polyesters.



$$\left[CH_2 - C(C_nH_{2n+1})(C(=O)-O-CH_3) \right]_m$$

Figure 13. Chemical formula of the polymethyl (α-n-alkyl) Acrylate samples. For n=1, the sample is called C1, for n=3, C3 etc…

Conclusion and Perspectives:

In this work, we have studied some semi-rigid polyesters according to the "strong-fragile" concept. For the three DP1.i samples, we found a thermodynamically "strong" and kinetically "fragile" behaviour. On one hand, by comparing our results with those obtained from other glass-forming liquids leading to linear polymers, we conclude that, the more rigid the main chain, the "stronger" the kinetic and thermodynamic behaviour. We plan to further prove this by substituting the biphenyl group in the main chain by the terphenyl group. On the other hand, the influence of the length of the lateral chain on the kinetic aspect is the same for the DP1.i family as for the polymethyl (α-n-alkyl) acrylate family, for a carbon number varying from 1 to 3. In the future, we will study the DP1.4, DP1.5 and DP1.18 samples according to the "strong-fragile" concept to confirm our assumption on the influence of the lateral chain on the relaxation behaviour at the glass transition.

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