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Thermal Properties of Aromatic Polycarbonates Copolymers Based on Bisphenol A and Tetramethyl Bisphenol A

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Summary: Statistical copolycarbonates containing different bisphenol A/tetramethyl bisphenol A (BPA/TMBPA) molar ratios were synthesized by polycondensation reaction between a mixture of the two bisphenols and phosgene. The reaction conditions were selected for producing polymers having comparable molecular weights ($\overline{M}_n \approx 9000$ g/mol) but different composition, and the same composition but different molecular weights.
The calorimetric properties of the products were investigated by differential scanning calorimetry (DSC) and dynamical-mechanical thermal analysis (DMTA). In particular, the effect of the copolymers molecular characteristics on the glass transition temperature (T_g) and the related relaxation processes were studied.
DMTA was employed for evaluating the effect of macromolecular structure on the γ low temperature relaxation peak.

Keywords: copolymers; enthalpy relaxation; glass transition temperature; polycarbonate

Introduction

Understanding the correlation between structure and properties, is a fundamental requisite for tailoring the performances of the polymeric materials, as a function of the final application. In the case of aromatic polycarbonates, the knowledge of these relationships is essential to design high performance materials that could be employed in the field of optical devices for data transport and storage [1].

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In this work the thermal properties of aromatic polycarbonates, synthesized starting from bisphenol A (BPA) and/or tetramethyl bisphenol A (TMBPA), were studied. In particular, the influence of polymer chemical structure and average molecular weight on the glass transition temperature (T_g) was investigated by differential scanning calorimetry (DSC) and the experimental data were compared to the Fox and Fox-Flory equations [2,3].

Since amorphous polymers below their T_g are not at equilibrium and their structures continuously relax in attempt to reach the equilibrium state, the structural recovery behaviour of the materials having the same $\overline{M}_n$ but different BPA/TMBPA molar ratio was characterized on the basis of the Tool-Narayanaswamy-Moynihan (TNM)/Kohlrausch-Williams-Watts (KWW) model [4]. In the model there are four independent parameters: the apparent activation energy (Δh^*), the non-linearity parameter (x), the non-exponentiality parameter (β) and the pre-exponential factor (τ_0). Experiments at different cooling rate [5] were carried out to evaluate Δh^* and an estimation of x and β was proposed using the normalized upper peak height [6]. The glass transition phenomena were also interpreted in the light of the fragility concept originally proposed by Angell [7]. The Δh^* parameter of the model was discussed in term of the relationship between relaxation and copolymer composition.

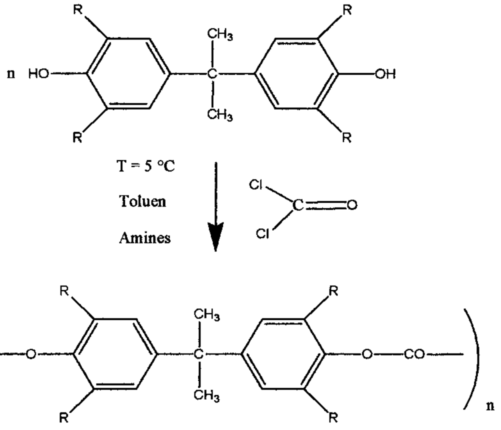
Finally, the macromolecular structure influence on low temperature γ transition was studied by dynamical-mechanical thermal analysis (DMTA).

Result and discussion

1. Materials

Homo-polycarbonates and statistical copolycarbonates containing different bisphenol A/tetramethyl bisphenol A (BPA/TMBPA) molar ratio were synthesized by polycondensation reaction between bisphenol(s) (or a mixture of two) and phosgene. The reactions (see scheme) were carried out at 5°C in toluene, using amines as acid acceptors [8]. The reaction conditions were selected for obtaining materials with different BPA/TMBPA content but analogous number average molecular weight ($\overline{M}_n \approx 9000$ g/mol), or same composition but different $\overline{M}_n$; this is essential if the effect of the macromolecular structure and molecular weight on thermal properties must be studied.

The composition of all copolymers was evaluated by ^{1}H-NMR and FT-IR spectroscopy while gel permeation chromatography (GPC) and viscosity measurements were carried out to determine the molecular masses.



Where R = H or CH_3

Scheme

The molecular characteristics of some synthesised polymers are summarized in Table 1.

Table 1. Molecular properties of polycarbonates synthesized.

Sample	BPA[a]	TMBPA[a]	$\overline{M}_n$ [b]	$\overline{M}_w$ [b]
	%-mol	%-mol	g/mol	g/mol
P-TBPA	-	100	9060	18830
P-TBPA	-	100	4970	9370
P-TBPA/BPA 50/50	50	50	5980	9640
P-TBPA/BPA 50/50	50	50	8020	18820
P-TBPA/BPA 50/50	50	50	8470	23820
P-TBPA/BPA 05/95	95	50	9420	20820
P-BPA	100	-	2370	4110
P-BPA	100	-	12000	22600
P-BPA	100	-	18700	31000
P-BPA	100	-	23000	38400

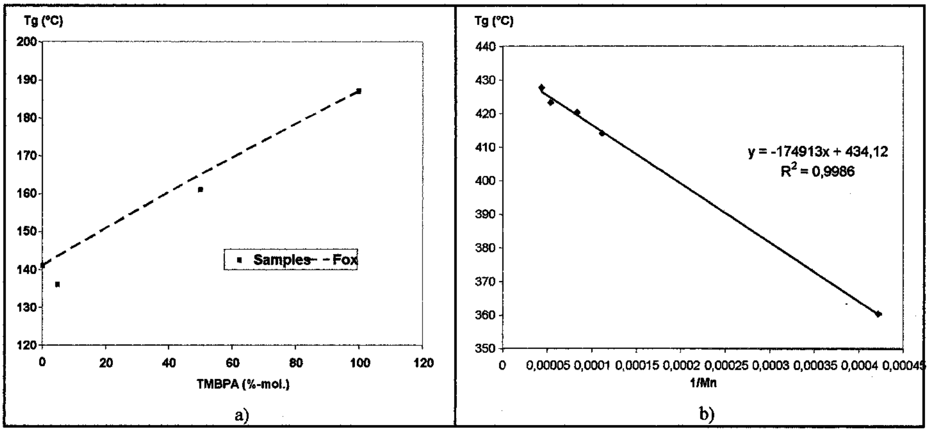
[a] calculated from ^{1}H-NMR spectra.
[b] GPC data evaluated using polystyrene standards.

2. Thermal properties and glass transition phenomena of materials

2.1. Molecular structure and T_g

The influence of copolymer composition and number average molecular weight on glass transition temperature was studied by DSC. In Figure 1.a the T_g values of the copolymers having $\overline{M}_n \approx 9000$ g/mol were plotted as a function of TMBPA content and in the same figure the experimental data were compared with the Fox prevision [2]. Higher stiffness of the polymeric chains was observed when the tetrametyl bisphenol A content increases, being 136°C, 161°C and187°C the T_g values for P-TBPA/BPA 5/95, P-TBPA/BPA 50/50 and P-TBPA, respectively. It should be noticed that the difference between the experimental and theoretical data is substantially due to the lower T_g value of 5/95 P-TBPA/BPA copolymer (136 °C), respect to BPA homopolymer (140 °C).

The specific heat capacity of glass transition increases with tetrametyl bisphenol A content, too. In fact ΔC_p of 0.235 (J/g°C), 0.267 (J/g°C) and 0.270 (J/g°C) were obtained respectively for 5%-mol, 50%-mol and 100%-mol of TMBPA.



a) b)

Figure 1. a) effect of TMBPA content on the T_g and the Fox prevision; b) effect of $\overline{M}_n$ on T_g of polycarbonates of bisphenol A (P-BPA).

The influence of number average molecular weight on T_g for materials with the same composition has been also evaluated. In general, for all materials, T_g increases with $\overline{M}_n$ until an asymptotic value ($T_g(\infty)$) is attained and the observed T_g does not vary with the molecular weight. This is expressed in the following equation, given by Fox and Flory [3], with the limit of an overestimation of $T_g(\infty)$ for a material having high molecular weight [9]:

$$T_g = T_g(\infty) - k/\overline{M}_n \qquad (1)$$

where $T_g(\infty)$ is the limiting T_g at high molecular weight and k is a constant related to the volume of chain ends.

In Figure 1.b the T_g as measured by DSC is plotted as a function of $1/\overline{M}_n$ for polycarbonate of bisphenol A (P-BPA). The slopes and intercepts evaluated with equation (1) for samples containing 0, 50 and 100 mol-% of TMBPA are summarized in Table 2.

Table 2. *k* parameter and $T_g(\infty)$ evaluated using the Fox-Flory equation.

Copolymer	***$k\cdot 10^{-5}$*** ***(gK/mol)***	***$T_g(\infty)$*** ***(K)***
P-BPA	1.75	437
P-TBPA/BPA 50/50	1.70	453
P-TBPA	1.51	477

It should be observed that k decreases if the TMPBA content increases, suggesting that the free volume of the end groups plays progressively a less role. This fact could be explained considering that if the chain stiffness increases the end groups mobility decreases.

2.2. Enthalpy relaxation

The procedure adopted here for the analysis of DSC data follows a well-recognized approach. It is assumed that the relaxation time(s) (τ) for enthalpy relaxation depends on both the temperature (T) and the structure of the glass, identified by its fictive temperature (T_f), according to the so called **Tool-Narayanaswamy-Moynihan** (TMN) equation [10]:

$$\tau(T, T_f) = \tau_0 \exp\left[\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f}\right] \qquad (2)$$

where τ_0 is the value of τ in equilibrium at infinitively high temperature, Δh^* is the apparent activation energy for enthalpy relaxation, and x $(0 \leq x \leq 1)$ is the non-linearity parameter identifying the relative contributions of temperature and structure to the relaxation(s) time.

Equation (2), though, is written for a single relaxation time and it is well known that a distribution of the relaxation times is required to describe the relaxation kinetics [11]. A continuous spectrum can be introduced by means of the stretched exponential function or **Kohlrausch-Williams-Watt** (KWW) equation [12]:

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right]. \qquad (3)$$

The exponent β ($0 \leq \beta \leq 1$) is the non-exponentiality parameter inversely proportional to the width of the corresponding distribution of relaxation times, and τ is given by eq.(2).

Equations (2) and (3) when combined with a constitutive kinetic equation in which the rate of approach to equilibrium is proportional to the departure from equilibrium, are sufficient to describe the response of a glass to any thermal history.

The intention, here, is to evaluate the apparent activation energy Δh^*, introduced in (2), in order to estimate the effect of the copolymer composition on the relaxation processes. In this respect, a set of experiment in which the sample is cooled at different constant rates before immediately scanning in DSC is required. As example, Figure 2.a shows the behaviour of P-TBPA. The dependence of the T_f from the cooling rate q_c may be written as follows [13]:

$$-\frac{\Delta h^*}{R} = \frac{d\left[\ln(|q_c|)\right]}{d\left[1/T_f\right]} \qquad (4)$$

The T_f for a given cooling rate is obtained by the equal areas method [14] and Δh^* is then evaluated from the slope of the plot of $\ln[|q_c|]$ vs $[1/T_f]$, as illustrated in Figure 2.b. The results for all the samples tested are summarized in Table 3.

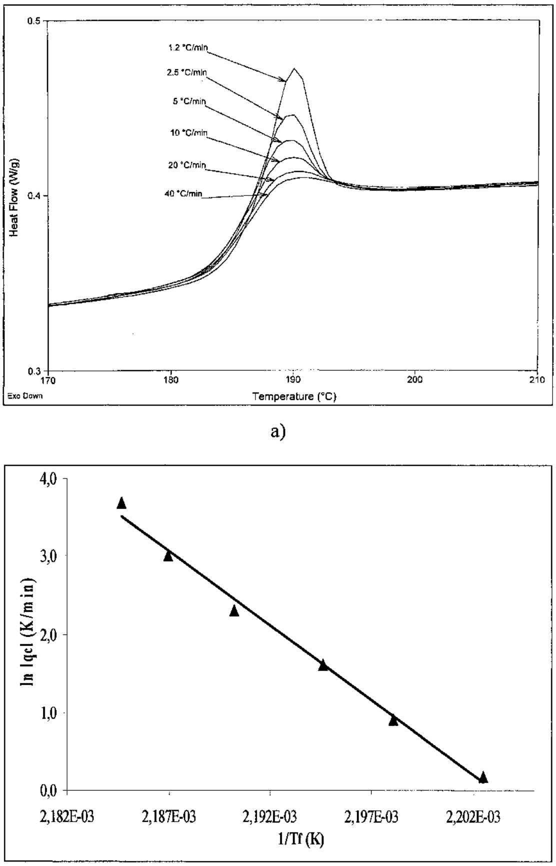
Table 3. Δh^* evaluated for copolymers having different composition.

Copolymer	***M_n* (g/mol)**	***Δh^** (kJ/mol)**	***R^2***
P-TBPA	9060	1592	0.992
P-TBPA/BPA 50/50	8470	1522	0.992
P-TBPA/BPA 05/95	9420	1415	0.996

Since the relaxation is a highly co-operative process, the measured apparent activation energy is not in itself representative of the activation energy of the fundamental molecular process. In fact, it can be shown [15] that the primary activation energy E_a of the fundamental molecular process is related to the apparent activation energy through the non-exponentiality parameter:

$$E_a = \Delta h^* \beta \qquad (5)$$

The implication is that for any given primary process, the broader the distribution of the relaxation times is, the greater will be the co-operativity necessary between molecular segments participating in the relaxation, and the greater will be the apparent activation energy.



a)

b)

Figure 2. a) Heating scans at 10°C/min for P-TBFA sample (6.5 mg) cooled at the rates indicated against each curve and immediately reheated in the DSC. All the cooling and reheating scans, concerning an experiment, were run on the same sample. Only a part of the complete scans from 137 to 330°C are shown here for clarity. b) Plot of ln(cooling rate) vs reciprocal fictive temperature for cooling traces shown in a). The full line represents the least-squares fit to the data.

As reported in Table 3, an increase of the T-PBFA content in the copolymer correspond to an increase of Δh^* value. These results could be also interpreted in terms of fragility concept, developed by Angel in 1985 [16] for classifying the simple glass forming liquids behaviours. In this view, strong liquids are characterised by stable structure and properties that do not dramatically change from the liquid state to the glassy state. On the other hand, for fragile liquids such structures are unstable and properties changes are more evident. This is valid for the thermodynamic response (e.g. specific heat capacity) and the transport properties (e.g. viscosity).

Generally, the fragility can be defined from the relaxation time associated with the glass transition, plotted as a function of T_g\T: in this representation, it describes the departure from the linear Arrhenius behaviour (strong liquid). The fragility parameter (*m*) corresponds to the limiting slope of the curve described above. While it is known that *m* increases with T_g [17] and the transition temperatures of P-TBFA/BFA 5/95, P-TBFA/BPA 50/50 and P-TBPA are respectively 136°C, 161°C and 187°C, we can deduce that at higher content of TMPBA in the copolymers corresponds a higher fragility.

In this respect, the experimental data reported in Figure 3 show an increase both of ΔC_p and enthalpy relaxation peak, going from 5% to 100% of TMPBA. These increase of fragility with the number of the methyl groups can be attributed to the modified ability for intermolecular coupling or cooperativity due to the introduction of steric constraints. In fact, as Plazeg and Ngai pointed out [18], there is a clear correlation between fragility and cooperativiy parameter determined in the coupling theory. In this view, compact chemical structures with less steric hindrance will be less fragile than other will.

An estimation of the non-linearity (x) and non-exponentiality (β) parameters introduced in equations (2) and (3) is also proposed. The same set of cooling rate experiments for the evaluation of Δh^* may be used to estimate the parameters β. As shown in Figure 2.a, for each cooling rate the heating scan displays the so-called upper peak [19].

The normalized heat capacity ($C_{p,u}^N$) at the upper peak temperature (T_u) can be evaluated using the definition of the normalized heat capacity (C_p^N) reported in the following equation:

$$C_p^N(T) = \frac{C_p(T) - C_{p,g}(T)}{\Delta C_p} \qquad (6)$$

where ΔC_p is the heat capacity increment between the glassy and liquid state. Since $C_{p,l}$ and $C_{p,g}$ are both to a certain extent temperature dependant, the evaluation of ΔC_p needs to be made at a specified temperature. Here, ΔC_p was found at the fictive temperature of unannealed samples cooled at 10°C/min.

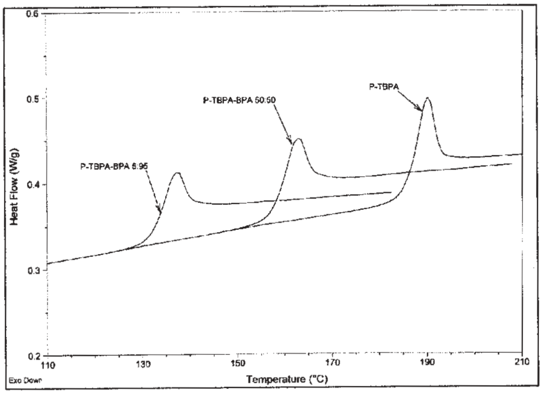


Figure 3. Comparison of the heating scans at 10 °C/min of the bis phenol A (BPA) and tetramethyl bisphenol A (TMBPA) copolymers cooled at 1.2 °C/min.

The magnitude of C_p^N at the upper peak depends on the ratio of cooling rate (q_c) to heating rate (q_h), on the parameter β, and, to a lesser extent, on the parameter x. The theoretical dependence of $C_{p,u}^N$ on $\log(|q_c|/q_h)$ for various combination of values of β and x [19] are reported in Figure 4.a and 4.b, while experimental curves relative to P-TBPA, P-TBPA/BPA 50/50 and P-TBPA/BPA 5/95 are reported in Figure 4.c. By comparing experimental data with theoretical curves, we can estimate that β and x for all analyzed samples lie in the range: $x<0.4$ and $0.456<\beta<0.6$. It should be noted that the $C_{p,n}^N$ curve of the P-TBPA is the highest, while those related to P-TBPA/BPA 50/50 and to P-TBFA/BPA 5/95 are nearly superimposed, suggesting a higher β value for the homopolymer.

Other methods of analysis to evaluate x and β values are reported. The results of a three parameters curve-fitting method reported in Table 4 confirm our previously estimation. These values are obtained minimizing the sum of squared differences between the experimental and predicted $C_p^N(T)$, using a home-made FORTRAN program [20,21].

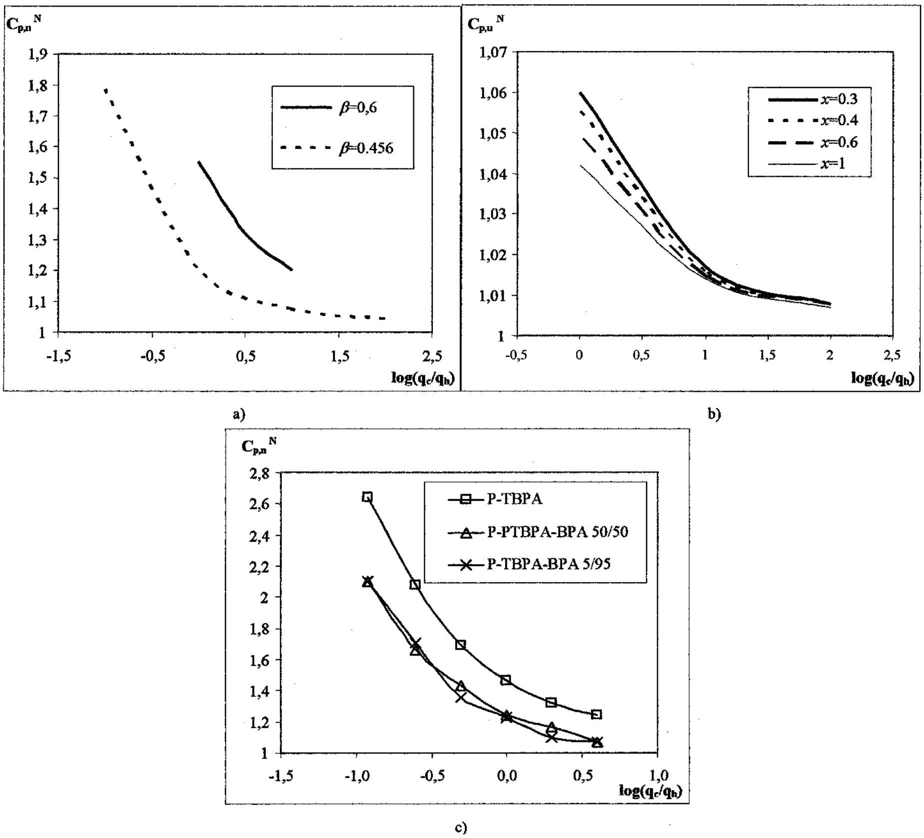


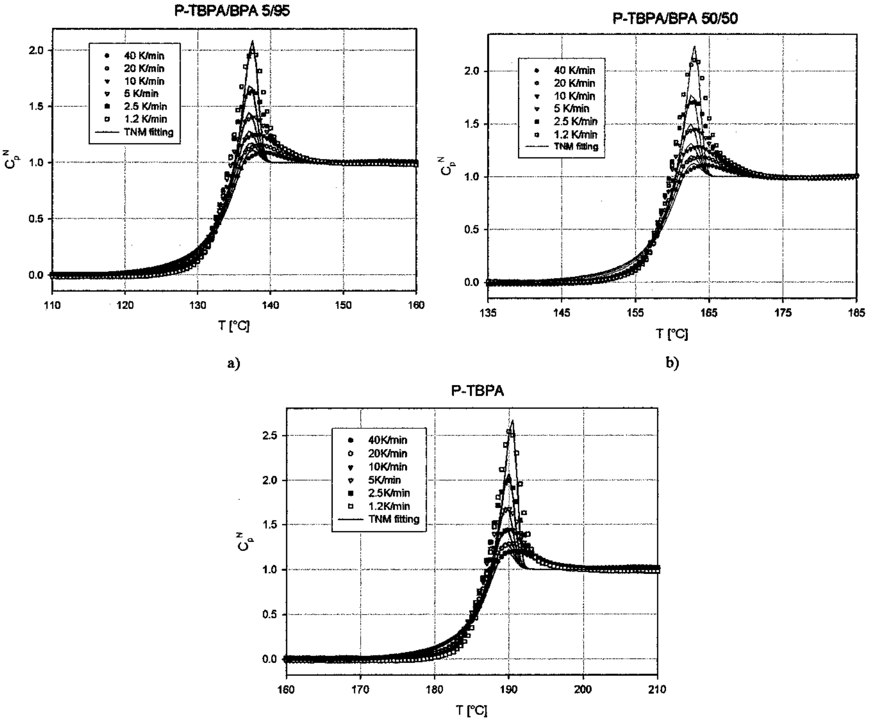
Figure 4. a) The theoretical dependence of $C_{p,u}^N$ on $\log(|q_c|/q_h)$ for various combination of values of β and x=0,4 [19]. b) The theoretical dependence of $C_{p,u}^N$ on $\log(|q_c|/q_h)$ for various combination of values of x and β=0.3 [19]. c) Experimental curves of $C_{p,u}^N$ on $\log(|q_c|/q_h)$ relative to P-TBPA, P-TBPA/BPA 50/50 and P-TBPA/BPA 5/95. For each material ΔC_p of equation (6) was found at the fictive temperature of unannealed sample cooled at 10°C/min.

Table 4. x, β and τ_0 evaluated for copolymers with different composition.

Copolymer	***x***	***β***	***-Ln(τ_0) (min)***	***R^2***
P-TBPA	0.265	0.521	418.3	0.983
P-TBPA/BPA 50/50	0.268	0.471	424.8	0.982
P-TBPA/BPA 05/95	0.287	0.465	419.5	0.988

The predicted and the experimental $C_p^N(T)$ relative to P-TBPA/BPA 5/95, P-TBPA/BPA 50/50 and P-TBPA are reported in Figure 5.a, 5.b and 5.c, respectively. It should be noted that all the experimental data are well fitted except the final part of the relaxation peak, where a mismatch can be clearly observed. This is probably due to a bi-modal distribution of the relaxation times, revealed by the non-symmetric shape of the peaks. In order to improve our model prediction, a modified TNM modelling procedure that take in account a bi-modal distribution of the relaxation times is in progress.

On the other hand, with the peak shift method an overestimation of x values, respectively 0.48, 0.48 and 0.45 for P-TBPA/BPA 5/95, P-TBPA/BPA 50/50 and P-TBPA, is obtained. The limit of this method was previously described by McKenna and co-worker [22].



a) b)

c)

Figure 5. Normalized heat capacity (C_p^N) vs. temperature (T) during heating at 10°C/min for P-TBFA/BPA 5/95(a), P-TBFA/BPA 50/50 (b), P-TBFA (c), cooled at the rates indicated in the legends. The keys represent experimental C_p^N heating curves, while solid lines are the C_p^N heating curves calculated from the three parameters curve-fitting procedure.

2.3. Effect of structure on γ transition

DMTA analysis of homopolymers and copolymers was performed at different frequencies (0.05 to 50 Hz) and temperatures (-150 °C to 140 °C). All materials evidenced a secondary relaxation (γ) below glass transition, in the low temperature range. The γ peak temperature presented a marked increase on increasing TMPBA content: T_γ = -95 °C, -93 °, -35 °C, + 60 °C (at 1.58 Hz) were recorded for P-BPA, 5/95 and 50/50 P-TBPA/BPA, P-TBPA respectively (Figure 6).

γ transition in P-BPA is attributed to cooperative motions of chain segments with a correlation distance of about 7 monomeric units [23]. As long as TMBPA units in the copolymer are closely spaced (less than about 7 BPA units) a marked increase of chain stiffness even in short range motions is observed as indicated by the T_γ shift.

In the 50/50 P-TBPA/BPA copolymer, a γ peak wider than in homopolymers was also observed (Figure 6). This was attributed to a distribution in the length of the monomeric units sequences as resulting from the random copolymerization reaction.

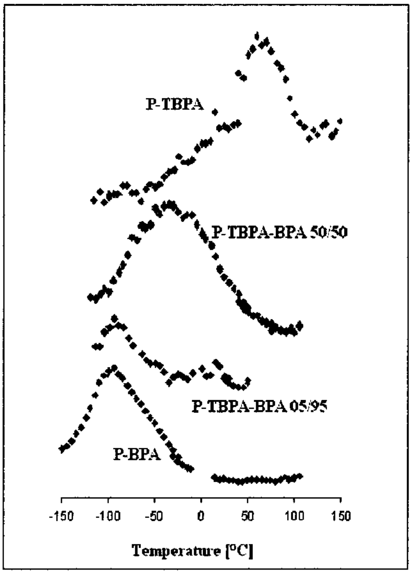


Figure 6. Tan δ peaks in the γ transition region of the copolymers at 1.58 Hz.

Conclusions.

Statistical copolycarbonates containing different bisphenol A/tetramethyl bisphenol A molar ratios were synthesized by stepwise polymerization. Products having analogous number average molecular weight but different TMBPA content showed higher T_g when tetramethylated monomer content increases; a linear trend of T_g versus $\overline{M}_n$ was observed. This clearly suggests that a increment of macromolecular stiffness occurs increasing the tetrametylated unit quantity.

This is also confirmed by the experimental values of Δh^* which suggest the increase of the methyl groups introduces a steric constraints modifying the ability for intermolecular coupling or cooperativity.

An estimation of non-linearity and non-exponentiality parameters was performed comparing the theoretical curves of the normalized upper peak height with the experimental data. The estimated range for these parameters are in good agreement with the values obtained by fitting method, already in progress.

The presence of tetramethylated units in the macromolecular chain strongly affects the shape and the position of the γ low temperature relaxation peak. In detail, wider peaks shifted to higher temperature are observed if the TMPBA content is increased.

[1] G.Kampf, D.Freitag, W.Witt Angew.Makromol.Chem. **1990**, 183, 243.
[2] T.G. Fox, Bull.Am.Phys.Soc. **1956**, 1, 123.
[3] T.G. Fox, P:J. Flory, J.Appl.Phys. **1950**, 21,581.
[4] J.M. Hutchinson, Prog.Polym.Sci. **1995**, 20, 703.
[5] J.M. Hutchinson, S.Smith, B.Horne, G.M.Gourlay, Macromolecules **1999**, 32, 5046.
[6] J.M. Hutchinson, M. Ruddy, J.Polym.Sci.,Polym.Phys.Ed. **1990**, 28, 2127.
[7] J.M. Hutchinson, Polym.Intern. **1998**, 47, 56.
[8] Italian P. MI2003A000542 (**2003**) Università degli Studi di Brescia M. Penco, L. Sartore, A. Lazzeri, L. Di Landro.
[9] J.M. Cowie, Eur.Polym.J. 1975, 11,297.
[10] A.Q. Tool, J.Am.Ceram.Soc. **1946**, 29, 240.
[11] A.J.Kovacs, Fortschr.Hochpolym.Forsch. **1963**, 3, 394.
[12] G.Williams, D.C.Watts, Trans. Faraday Soc. **1970**, 66, 80.
[13] A.J.Kovacs, J.J.Aklonis, J.M.Hutchinson, A.R.Ramos, J.Polym.Sci.Phys.Ed. **1979**, 17,1097.
[14] C.T.Moynihan, A.J.Easteal, M.A.DeBolt, J.Tucker, J.Am.Ceram.Soc. **1979**, 59, 12.
[15] K.L.Negai, Comm.Solid State Phys. **1980**, 9, 141.
[16] C.A.Angel in K.Ngai & G.B.Wright, Relaxation in complex systems **1985**, p.3. Springfield,VA: National Technical Information Service, US Department of Commerce.
[17] S.L.Simon, D.J.Plazek, W.Sobieski, E.T.McGregor, J.Polym.Sci. Part B:Polym.Phys. **1997**,35,929.
[18] D.J.Planzek, K.L.Ngai, Macromolecules **1991**, 24, 1222.
[19] J.M.Hutchinsons, M.Ruddy, J.Polym.Sci., Polym.Phys.Ed. **1990**, 28, 2127.
[20] A. D'Amore, F. Caputo, L. Grassia, M. Carrelli, Composites Part A-Applied Science and Manufacturing. **2004**, in press
[21] Y. Han, A. D'Amore, G. Marino, L. Nicolais, Materials Chemistery and Physics. **1998**,55,155-159
[22] Y.Zheng, S.L.Simon, G.B.McKenna, J.Polym.Sci. Part B:Polym.Phys. **2002**, 40, 2027.
[23] C. Xiao, A.F. Yee, Macromolecules **1992**, 25, 6800.