Thermochimica Acta, 105 (1986) 149–160
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EFFECT OF THE SIDE CHAIN STRUCTURE ON THE GLASS TRANSITION TEMPERATURES OF SOME POLY(THIOCARBONATE)S

M. YAZDANI-PEDRAM, E. SOTO, L.H. TAGLE, F.R. DIAZ, L. GARGALLO and D. RADIĆ

Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 6177-Santiago (Chile)

(Received 4 February 1986)

ABSTRACT

A series of poly(thiocarbonate)s with aliphatic, aromatic and cycloaliphatic side groups has been prepared and the glass transition temperatures (T_g)s of these polymers were measured by differential scanning calorimetry (DSC). The magnitude of the T_g was related to the bulkiness, flexibility, and polarity of the pendant groups attached to the polymer main chain. A general decrease in T_g values is observed when these polymers are compared with the corresponding poly(carbonate)s analogues. Theoretical calculation of T_g for some of the polymers were carried out using the method described by Van Krevelen et al. These values are in fair agreement with the experimental values. The critical value of the chain length at which T_g becomes constant (T_g^∞) was calculated for all the polymers using the relation proposed by Cowie. It was found that the molecular weights of the polymers are too low for T_g to become independent of the chain length.

INTRODUCTION

Poly(thiocarbonate)s are a new family of amorphous polymers which in many aspects can offer parallel properties and applications to poly(carbonate)s. The aim of this work is to demonstrate essentially how the glass transition temperatures of these polymers can be controlled by introducing structurally-different side groups into the backbone of the polymer. The flexibility, bulkiness, and polarity of pendant groups attached to the main chain can play an important role in determining T_g since this temperature indicates the onset of long range cooperative chain motion in the polymer sample. It has been observed that the size, polarity and flexibility of the side groups can alter the T_g values of poly(carbonate)s [1]. The thermal behaviour of poly(thiocarbonate)s has not been reported in the literature. In this work a series of poly(thiocarbonate)s having different side groups has been prepared and their glass transition temperatures have been measured by DSC.

0040-6031/86/$03.50

EXPERIMENTAL

Monomer and polymer preparations and characterizations

Diphenols were obtained by condensation of phenol with the corresponding aldehyde or ketone according to the procedure of McGreal et al. [2].

Poly(thiocarbonate)s were synthesized by phase transfer catalysis from the diphenols and thiophosgene using several quaternary ammonium and phosphonium salts in dichloromethane as solvent. The syntheses and characterizations of these polymers have been described in detail in our previous publication [3].

Molecular weight determinations

The weight average molecular weights ($\overline{M}_w$), the number average molecular weights ($\overline{M}_n$) and the polydispersity index ($\overline{M}_w/\overline{M}_n$) of the polymers were determined by size-exclusion chromatography (SEC), using a Perkin-Elmer high performance liquid chromatograph (HPLC) equipped with a 6000-Psi (0.84 Pa) pump, a Perkin-Elmer differential refractometer model LC-25 and an injector of 175 μl. Three Water Associates Ultra Styragel™ Columns (10^3 Å, 10^4 Å and 10^5 Å) in series were used. Tetrahydrofuran was used as eluent and the flow rate was 1 ml min^{-1}. The columns were first calibrated with standard polystyrene samples of narrow molecular weight distribution. A calibration curve of the type $\log M = f(V_e)$, where V_e is the peak elution volumes for polystyrene standards were used. The $\overline{M}_w$ and $\overline{M}_n$ values of the polymers were calculated with the aid of a computer program based on normalization of the chromatograms [4]. It has been shown that the calibration curve obtained from polystyrene fractions with narrow molecular weight distribution is of adequate precision for determining molecular weights of bisphenol A-poly(carbonate)s [5].

Differential scanning calorimetry (DSC)

The glass transition temperatures (T_g) of polymer samples were measured using a Perkin-Elmer model DSC-1B differential scanning calorimeter. 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 a purge gas and thermograms were measured between 300 K and 500 K at scan rates of 16 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 (500 K) and quenched to the starting temperature in order to minimize differences in thermal history. The glass transition was located as 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 structures of poly(thiocarbonate)s studied are shown in Table 1 and are coded by numbers I–XVII. These polymers are further subdivided into four main groups (1–4) and will be refered to by their respective numbers or groups throughout.

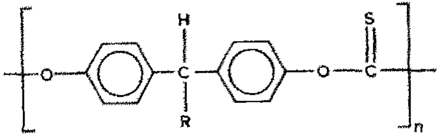
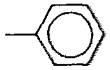
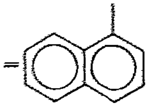
The thermal response of each polymer in the range 300 K–500 K was measured by DSC. Well-defined and reproducible glass transitions were observed for all polymer samples and the results are shown in Table 1. T_g values of the corresponding poly(carbonate)s taken from the literature [1] are also listed in Table 1 for comparison. In most cases the T_g values of poly(thiocarbonate)s are slightly lower than those of the corresponding polycarbonate analogue except for sample VII where the T_g value was markedly higher than the corresponding polycarbonate. These results agree with the rigidity factor σ found by us [6] for structure VII from dilute solution viscosity measurements. In all cases the steric hindrance parameter σ is lower for poly(thiocarbonate)s than for poly(carbonate)s. This has been explained in terms of the different contribution to the partial double bond character of the CO–O and CS–O groups. Moreover, a T_g value of 455 K was recently reported by Mikroyannidis [7] for this polycarbonate. This was measured by DSC at a heating rate of 20 K min^{-1}. This value is in agreement with our T_g value for this polymer determined under almost the same conditions and supports the explanation of Mikroyannidis.

Theoretical values of T_g for some of the structures studied (see Table 1) were calculated using the method described by Van Krevelen et al. [8]. These values are in fair agreement with experimental values. They can only be regarded as approximate values for poly(thiocarbonate)s since the contribution from the thiocarbonyl group has been assumed to be the same as that of the carbonyl group. In general, the variations of the experimentally obtained T_g values with the structure for poly(thiocarbonate)s is evident since we have chosen samples with reasonably comparable molecular weights. This should eliminate the effect of the molecular weight on the T_g value and consequently the predominant factor affecting T_g should stem from structural variations of the side groups. These variations include mainly the bulkiness as well as rigidity and polarity of the side groups.

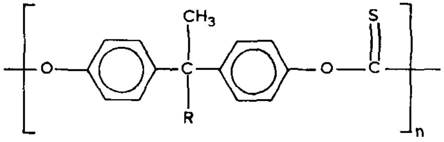
If the most important factor influencing T_g is considered to be the bulkiness of the pendant groups, which imposes steric restrictions on the rotation of the main chain, then the T_g values in each group should increase as the total volume of the side chains [9] increases (see Table 2). Exceptions arise when some degree of flexibility is introduced into the side chain of the

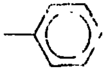
TABLE 1

Weight average molecular weights $\overline{M}_w$(GPC), number average molecular weights $\overline{M}_n$(GPC), polydispersity index $(\overline{M}_w/\overline{M}_n)$ estimated from GPC measurements, glass transition temperatures for poly(carbonate)s T_g(Pc), poly(thiocarbonate)s T_g(PTC) and the calculated T_g values T_g(calculated) for poly(carbonate)s

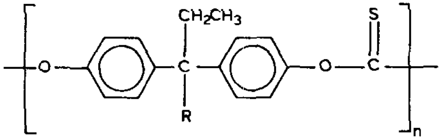
Polymer structure		T_g(K) (PTC)	T_g(K) (PC)	T_g(K) (calculated)	$\overline{M}_{w(GPC)}$	$\overline{M}_{n(GPC)}$	$(\overline{M}_w/\overline{M}_n)_{GPC}$
Group I							
							
(I)	R = H	368	420	414.5	–	–	–
(II)	R = $-CH_3$	380	403	403.4	25800	10400	2.48
(III)	R = $-CH_2CH_3$	377	–	377.6	19100	9000	2.12
(IV)	R = $-CH_2CH_2CH_3$	400	396	357	33700	15300	2.20
(V)	R = $-CH(CH_3)_2$	408	422	417.8	21600	12500	1.73
(VI)	R = $-CH(CH_2CH_3)_2$	421	–	–	36300	14000	2.60
(VII)	R = 	452	394	–	–	–	–
(VIII)	R = 	464	–	–	5300	2900	1.82

Group 2



(IX)	R = $-CH_3$	411	418	377.6	27 400	19 300	1.42
(X)	R = $-CH_2CH_3$	375	407	357	33 400	14 500	2.30
(XI)	R = $-CH_2CH(CH_3)_2$	401	–	–	32 800	18 800	1.74
(XII)	R = 	454	449	–	27 200	14 400	1.89

Group 3



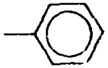
(XIII)	R = $-CH_2CH_3$	394	–	340	–	–	–
(XIV)	R = 	446	–	–	34 700	17 900	1.94

TABLE 1 (continued)

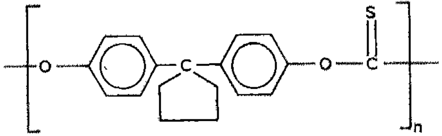
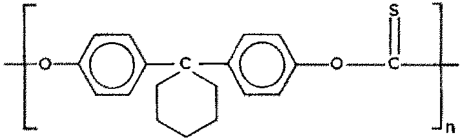
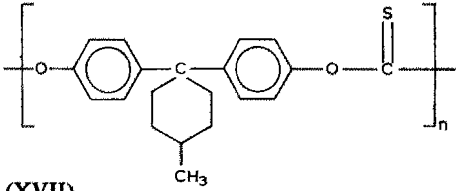
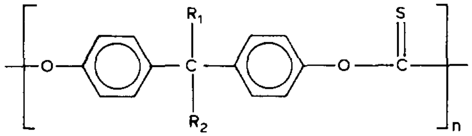
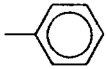
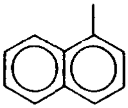
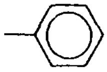
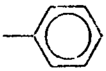
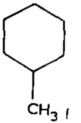
Polymer structure	T_g(K) (PTC)	T_g(K) (PC)	T_g(K) (calculated)	$\overline{M}_{w(GPC)}$	$\overline{M}_{n(GPC)}$	$(\overline{M}_w/\overline{M}_n)_{GPC}$
Group 4						
 (XV)	352	440	–	–	–	–
 (XVI)	428	448	–	28 900	16 300	1.77
 (XVII)	441	–	–	42 400	20 100	2.11

TABLE 2

Volume equivalent [a] [9] values of side chains R_1 and R_2 and Bondi ring volumes [b] for poly(thiocarbonate)s with general structure



Polymer code	Side chain structure		V_1 [a] (cm^3 mol^{-1})	V_2 [a] (cm^3 mol^{-1})	V_1+V_2 (cm^3 mol^{-1})
(I)	$R_1 = H$	$R_2 = H$	3.7	3.7	7.4
(II)	$R_1 = H$	$R_2 = -CH_3$	3.7	25.9	29.6
(III)	$R_1 = H$	$R_2 = -CH_2CH_3$	3.7	48.1	51.8
(IV)	$R_1 = H$	$R_2 = -CH_2CH_2CH_3$	3.7	70.3	74.0
(V)	$R_1 = H$	$R_2 = -CH(CH_3)_2$	3.7	70.3	74.0
(VI)	$R_1 = H$	$R_2 = -CH(CH_2CH_3)_2$	3.7	114.7	118.4
(VII)	$R_1 = H$	$R_2 =$ 	3.7	92.3	96.0
(VIII)	$R_1 = H$	$R_2 =$ 	3.7	143.9	147.6
(IX)	$R_1 = -CH_3$	$R_2 = -CH_3$	25.9	25.9	25.9
(X)	$R_1 = -CH_3$	$R_2 = -CH_2CH_3$	25.9	48.1	74.0
(XI)	$R_1 = -CH_3$	$R_2 = CH_2CH(CH_3)_2$	25.9	92.5	118.4
(XII)	$R_1 = -CH_3$	$R_2 =$ 	25.9	92.3	118.2
(XIII)	$R_1 = -CH_2CH_3$	$R_2 = -CH_2CH_3$	48.1	48.1	96.2
(XIV)	$R_1 = -CH_2CH_3$	$R_2 =$ 	48.1	92.3	140.4
(XV)	-	$R_2 =$ 	-	46.6 [b]	46.6
(XVI)	-	$R_2 =$ 	-	56.8 [b]	56.8
(XVII)	-	$R_2 =$  CH3	-	56.8 [b]	82.7

[a] Volume equivalents taken from ref. 9.

[b] Bondi ring volumes taken from ref. 10.

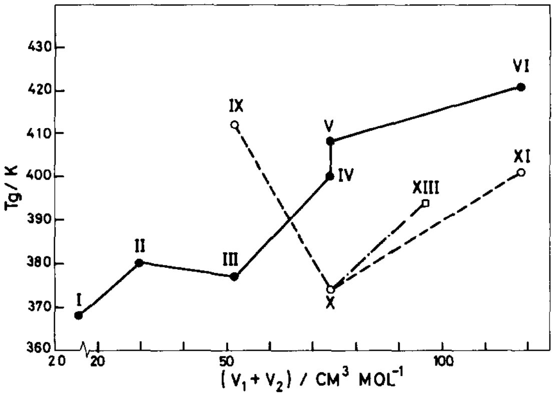


Fig. 1. Glass transition temperatures (T_g) as a function of total side chain volumes for polymers with aliphatic side chains. (●) Group 1; (○) group 2; (□) group 3.

polymer causing T_g to decrease. This effect can be seen clearly from Fig. 1 for samples III, X, XI and XIII where the T_g values of polymers with aliphatic side chains from groups 1, 2 and 3 are plotted against their total side chain volumes [9]. In either of these groups, polymers with one methylene unit in their lateral chains, have lower T_g values than their immediate analogues, although in these samples the volume of the side chain is larger than their preceding polymers. This is also true in the case of a polycarbonate sample belonging to group 2 (see Table 1, sample X) where the T_g value for this polymer is slightly lower than the preceding sample IX. Insertion of a methylene unit in the side chain of the polymer presumably acts as an internal plasticizer and depresses T_g. In polymers with longer aliphatic side chain a monotonic increase in T_g is observed where flexibility of the longer alkyl side group compensate its volume effect (see Fig. 1).

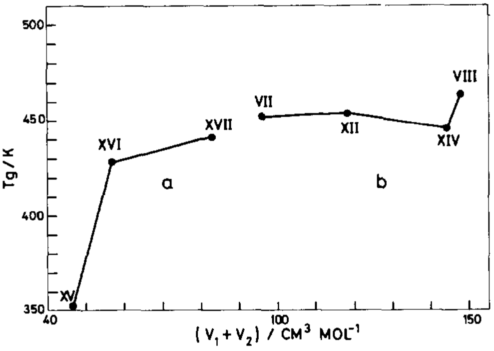


Fig. 2. Variation of the glass transition temperatures (T_g) of samples with (a) aromatic groups in the side chain and (b) alicyclic groups in the side chain as a function of total side chain volumes.

Figure 2 shows the variation of T_g with the total volume of the side chains in samples containing aromatic and alicyclic groups. For samples containing an aromatic side group, T_g increases with increasing volume of the aromatic group as well as total side chain volumes. For samples VII, VIII, XII and XIV the dependence of T_g on total volume of their side chains is shown in the right hand side of Fig. 2. The presence of a methylene unit in the side chain of sample XIV lowers its T_g value compared with samples VII and XII although the total volume of the side chains of this polymer is much larger than those of samples VII and XII. For the polymers with a saturated ring in the side chain (group 4) T_g increases with increasing ring size.

It is interesting to note that in the case of sample XVII where the cyclohexyl group has a methyl substituent there is an important increase in the T_g value when it is compared with sample XVI which contains only the cyclohexyl ring as the side group. This can be due to the increased volume of the side chain in XVII, and for the particular conformation of the 4-methylcyclohexyl group, according to the ^{1}H NMR spectra of the monomer.

Since polymers containing aromatic and alicyclic side chains show a similar relationship between T_g with the side group volume, we have shown the latter in the left hand side of Fig 2. We realize that the Bondi volumes for rings [10] shown in Table 2 are not comparable with volume equivalents [9] for aromatic and aliphatic groups since they are calculated by different methods. Since the cyclohexyl ring has a much larger volume than the phenyl group, those samples with phenyl groups in the side chain and those containing alicyclic rings can be presented in the same Figure for comparison purposes only. In other words a shift in volume for either of the structures does not affect the trend in T_g values observed for these polymers. However we suggest that the higher T_g values obtained for polymers with aromatic side groups, compared with their alicyclic analogues, could be due to the rigidity of the aromatic groups as well as some specific interactions between thiocarbonyl groups and aromatic groups which should lead to greater steric restriction thereby maintaining a high T_g value.

The dependence of the glass transition temperature on molecular weight for ten fractions of sample IX can conveniently be represented by the relation proposed by Flory and Fox [11]

$$T_g = T_g(\infty) - K_g M^{-1} \tag{1}$$

where T_g is the glass transition temperature for a given molecular weight $\overline{M}$, $T_g(\infty)$ is the glass transition temperature of infinitely large molecular weight and K_g is a constant characteristic of a given polymer.

The variation of T_g with molecular weight for ten fractions of sample IX is shown in Fig. 3. A reasonably linear dependence of T_g on molecular weight is observed. From this an extrapolated value of $T_g(\infty) = 435.6$ K (where T_g becomes independent of chain length) was obtained. This value is very near to that obtained for a fraction of sample IX with $\overline{M}_w = 2 \times 10^5$

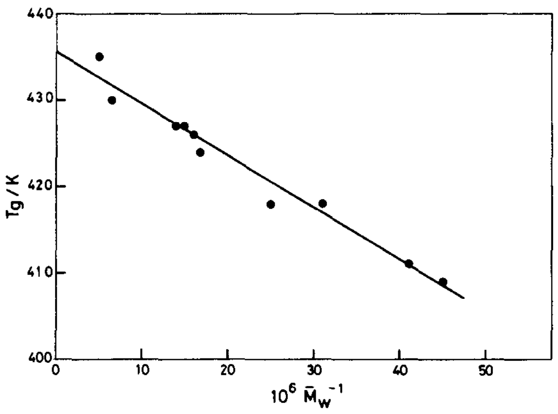


Fig. 3. Dependence of glass transition temperature T_g against $(1/\bar{M}_w)$ for ten fractions of sample IX.

($T_g = 435$ K) which indicates that the asymptotic value of T_g has been achieved for this particular fraction.

In order to estimate the critical value of the chain length at which T_g becomes constant ($T_g(\infty)$) for all polymers, the relation proposed by Cowie [12] was used

$$T_g(\infty) = 372.6 \log X_c - 595 \quad (2)$$

TABLE 3

Number average degree of polymerization ($\bar{X}_n$) and the critical number of chain atoms X_c values for poly(thiocarbonate)s

Sample code	$\bar{X}_n$	X_c [a]
(I)	–	64
(II)	40	69
(III)	33	68
(IV)	54	78
(V)	44	82
(VI)	45	89
(VII)	–	107
(VIII)	8	116
(IX)	71	84
(X)	51	67
(XI)	60	78
(XII)	43	109
(XIII)	–	75
(XIV)	51	103
(XV)	–	58
(XVI)	52	93
(XVII)	62	100

[a] Calculated by using the relation proposed by Cowie [9].

where X_c is the critical number of chain segments, either bonds or atoms. This relation was obtained by plotting T_g versus log X_c for all carbon backbone polymers, such as polystyrene, poly(α-methyl styrene), polydimethylsiloxane, etc. Cowie suggested that this relation should also be a reasonable guide for predicting the critical chain length of polymers with hetero-atoms in their backbone. The results obtained for poly(thiocarbonate)s are presented in Table 3. These results show that in all samples the degree of polymerization is not large enough to ensure that the asymptotic value of T_g is recorded. Indeed when the $T_g(\infty)$ value for the structure IX is introduced into Cowie's relation we obtain $X_c = 97$ which is near to the X_c value obtained for sample IX. This shows that the relation can be a working guide for predicting the critical value of chain length in a polymer containing hetero-atoms in the backbone.

CONCLUSIONS

It is concluded from this study that the glass transition temperatures of poly(thiocarbonate)s are in general lower than those of poly(carbonate) analogues. The T_g values for poly(thiocarbonate)s are greatly influenced by the rigidity, polarity, and total volume of the side chains. The T_g values of poly(thiocarbonate)s containing aromatic groups in the side chain are higher than those containing alicyclic rings. The dependence of T_g on molecular weight for ten fractions of sample IX derived from bisphenol-A can be described conveniently by the relation proposed by Flory and Fox. A reasonable linear dependence of T_g on molecular weight is obtained for this polymer and a value of $T_g(\infty) = 435.6$ K was estimated from the extrapolation of data to infinite molecular weight. The critical value of the chain length (X_c) at which T_g reaches its asymptotic value ($T_g(\infty)$) was estimated by using the relation proposed by Cowie. The results obtained showed that in all cases the molecular weight of the polymers studied here was not high enough for T_g to reach its asymptotic value.

ACKNOWLEDGEMENTS

We thank Dirección de Investigación (DIUC), Pontificia Universidad Católica de Chile and Fondo Nacional de Ciencias for financial support.

REFERENCES

1 I. Brandrup and E.H. Immergut (Eds.), Polymer Handbook, Wiley, New York, 1975.
2 M.E. McGreal, U. Neiderl and J.B. Neiderl, J. Am. Chem. Soc., 61 (1939) 345.

3 L.H. Tagle, F.R. Díaz, J.C. Vega and P.F. Alquinta, Makromol. Chem., 189 (1985) 915.

4 J.F. Rabek, Experimental Methods in Polymer Chemistry, ch. 32, p. 527, John Wiley and Sons, New York, 1983.

5 J. Brzezinski and Z. Dobkowski, Eur. Polym. J., 16 (1980) 85.

6 E. Soto, L.H. Tagle, F.R. Díaz, L. Gargallo and D. Radić, Eur. Polym. J., 22 (1986) in press.

7 J.A. Mikroyannidis, Eur. Polym. J., 21 (10) (1985) 895.

8 H.G. Weyland, P.J. Hoftyzer and D.W. Van Krevelen, Polymer, 11 (1) (1970) 79.

9 J.M.G. Cowie, Polymers: Chemistry and Physics of Modern Materials, International Textbook Co. Ltd., Guilford and London, 1973, p. 215.

10 A. Bondi, J. Phys. Chem., Ithaca, 68 (1964) 441.

11 T.G. Fox and P.J. Flory, J. Appl. Phys., 21 (1950) 581.

12 J.W.G. Cowie, Eur. Polym. J., 11 (1975) 297.