Substituent effect on the glass transition temperature of polyoxetanes

E. Pérez*, A. Bello, and J. M. Pereña

Instituto de Ciencia y Tecnología de Polímeros, Juan de la Cierva 3, E-28006 Madrid, Spain

Summary

The effect of the substituents on the glass transition temperature is analyzed for a series of polyoxetanes, with alkyl substituents in position 3. The results show a regular increase of that parameter with the Van der Waals volume of the linear substituents, although a departure from this trend seems to be observed for poly(3,3-dibutyloxetane), presumably because of the effect of internal plasticization. On the other hand, the increase of T_g for poly(3-terbutyloxetane) is specially high, as usual for branched substituents. The behaviour of the glass transition temperature along the series has been analyzed in terms of inter- and intramolecular interactions, concluding that the latter factor is the dominant contribution in determining the T_g in this group of polymers.

Introduction

The replacement of hydrogen atoms by different substituents is a widely used method in order to affect the physical properties of polymers. Particularly, the influence of pendent groups on the thermal properties is a subject of considerable interest. We have studied the thermal transitions of several polyoxetanes (1), substituted in position 3, with repeating unit:

$$-(- CH_2 - \overset{\overset{\displaystyle R_1}{|}}{\underset{\underset{\displaystyle R_2}{|}}{C}} - CH_2 - O -)_n-$$
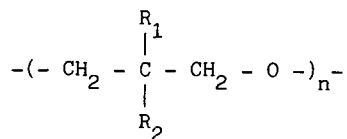
being R_1 and R_2 hydrogen atoms or alkyl substituents. The influence of the crystallization temperature on the melting behaviour and polymorphism of

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some of these polymers has been previously reported (1-5). We have also reported the values of the cohesive energy density, CED, and the unperturbed dimensions of several polyoxetanes (6-8), analyzing the effect of the substituents on those variables.

The purpose of this work is to extend that analysis to the study of a second order transition, the glass transition temperature, T_g, determined by means of differential scanning calorimetry (DSC).

Experimental

The polymers were all synthesized by cationic ring-opening polymerization of the corresponding monomers. The molecular weight of the samples used for this work was sufficiently high to expect no significant variations of T_g due to the influence of that parameter.

The glass transition temperatures were determined with a Mettler TA-3000 differential scanning calorimeter, at a heating rate of 10 degrees per minute, after quenching the samples from the melt to liquid nitrogen temperature at the highest cooling rate of the instrument. The calorimeter was calibrated with different standards, and the inflection point was taken as the glass transition temperature.

Results and Discussion

The DSC curves corresponding to some selected polyoxetanes, quenched from the melt to liquid nitrogen temperature to avoid crystallization of the sample, are shown in figure 1. An important feature from this figure is that the rate of crystallization is very different among polyoxetanes. Thus, unsubstituted polyoxetane (PTO) is capable of crystallizing during the residence time in the calorimeter (as well as the diethyl (PDEO), dipropyl (PDPO) and dibutyl (PDBO) derivatives) while other polyoxetanes, like the dimethyl (PDMO), ethyl-methyl (PEMO) and methyl-propyl (PMPO) derivatives exhibit a crystallization rate much smaller, in such a manner that they cannot crystallize in the calorimeter at 10 degrees per minute (after quenching from the melt). Thus, it can be observed in figure 1 that PTO presents not only the T_g at -71°C, but also a cold crystallization around -30°C and the subsequent melting around 20°C. On the contrary, PTBO, PDMO and PEMO show only the glass transition.

The corresponding values of T_g for the different polyoxetanes mentioned above are presented in Table 1, showing a regular increase with
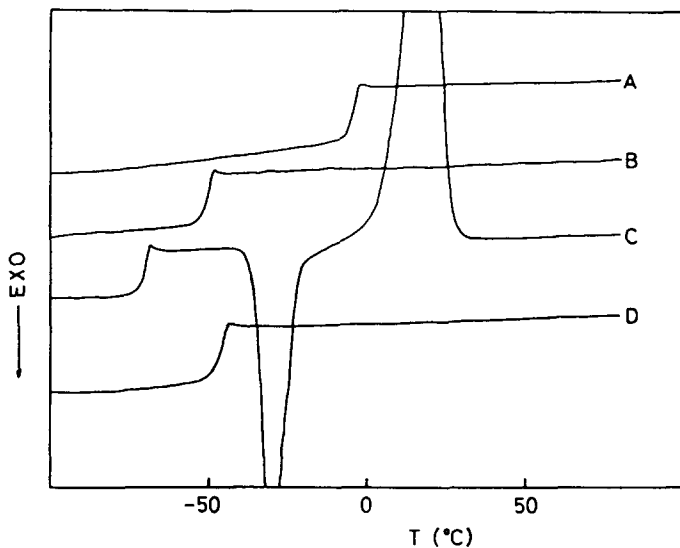
Fig. 1. DSC curves for several polyoxetanes quenched from the melt.
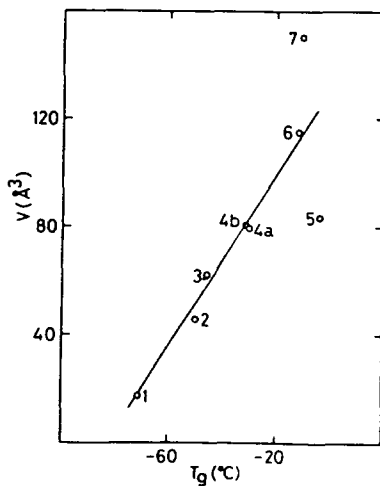A: PTBO; B: PDMO; C: PTO; D: PEMO.

Fig. 2. Plot of the glass transition temperature versus the Van der Waals
volume of the substituents for several polyoxetanes. 1: PTO;
2: PDMO; 3: PEMO; 4a: PDEO; 4b: PMPO; 5: PTBO; 6: PDPO; 7: PDBO.

Table 1: Glass transition temperature, T_g, cohesive energy density, CED, and characteristic ratio, $|r^2|_0/nl^2$, for several polyoxetanes

Polymer	$T_g(°C)$	CED (cal/cm^3)	$|r^2|_0/nl^2$
Poly(oxetane), PTO	−71	88.4	3.9 (9)
Poly(3,3-dimethyloxetane), PDMO	−50	62.4	4.2
Poly(3-ethyl,3-methyloxetane), PEMO	−46	64.0	−
Poly(3,3-diethyloxetane), PDEO	−30	62.4	−
Poly(3-methyl,3-propyloxetane), PMPO	−31	−	−
Poly(3,3-dipropyloxetane), PDPO (10)	−12	64.0	4.8
Poly(3,3-dibutyloxetane), PDBO (11)	−10	68.9	5.7
Poly(3-terbutyloxetane), PTBO	−4	70.6	−

the size of the linear substituents. This effect is clearly shown in figure 2, where the value of T_g is plotted against the Van der Waals volume (12) of the substituents. This representation is fairly linear and only PDBO and PTBO depart from the common straight line, a fact that will be analyzed later. The increase of T_g seems to reflect the influence of the volume of the substituents on the possibility of cooperative movements characterizing T_g. Thus, the behaviour of polyoxetanes is different from other series of polymers, where the influence of the substituents has been analyzed, namely poly(α-olefines) (13), poly(alkyl methacrylates) (14), poly(vinyl alkyl ethers) (14,15) or poly(alkyl itaconates) (16). All these series exhibit a continuous decrease on T_g beginning just on passing from the methyl to the ethyl derivative. It is true, however, that poly(alkyl methacrylates), poly(vinyl alkyl ethers) or poly(alkyl itaconates) are different from polyoxetanes in what those bear a flexible group between the alkyl fragment and the backbone. Thus, poly(α-olefines) are structuraly closer to polyoxetanes and in this series the increase on T_g with the substituent is found only for the first member (polypropylene in relation to polyethylene) decreasing later until the size of the linear substituent is big enough to produce lateral crystallization. The decrease on T_g has been ascribed to the "internal" plasticization effect (16) of

the flexible hydrocarbon chains as the length of the alkyl end increases.

However, this behaviour is not found in the polyoxetanes here studied, although a possible indication of the beginning of that effect may be the departure from the common straight line exhibited by PDBO, as shown in figure 2. Polyoxetanes with longer substituents should be studied in order to assure this point. On the other hand, PTBO also departs from the straight line, with a higher T_g in this case. However, this is a usual feature of branched substituents, and can be also observed in the other series of polymers mentioned above.

The behaviour of the glass transition temperature can be analyzed in terms of inter- and intramolecular interactions, which determine the value of T_g. The intermolecular contributions can be estimated from the cohesive energy density (CED) shown in Table 1. The values of this parameter are rather constant and only PTO presents a CED substantially. higher. This means that if the intermolecular interactions were the dominant, PTO should exhibit the highest T_g of the series, contrary to the experimental evidence reported in this work.

On the other hand, the intramolecular factors can be correlated with the unperturbed dimensions as expressed by the characteristic ratio $|r^2|_o/nl^2$ (17). This parameter, as shown in Table 1 for several polyoxetanes, displays a smooth increase with the volume of the substituent, that is similar to the observed variation on the glass transition temperature.

The main conclusion is, then, that the intramolecular factors, related to the restrictions for bond rotations, seem to be the dominant contribution in determining the glass transition temperature of polyoxetanes. The flexibility of the polyoxetane backbone, involving the ether group, and the four-bond repeating unit may be responsible for the particular behaviour when comparing to other series with only carbon atoms in the backbone.

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