

GLASS TRANSITION TEMPERATURES OF SUBSTITUTED POLYOXETANES

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ABSTRACT

The glass transition temperature, T_g , of several polyoxetanes, with alkyl substituents in position 3, has been determined by differential scanning calorimetry. The results show a regular increase of that parameter with the size of the substituents, and only for the case of the dibutyl derivative it seems that this trend is not followed, presumably because of the effect of internal plasticization. On the other hand, the increase on T_g for poly(3-tertbutyl oxetane) 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 last factor is the most decisive in determining the T_g in this group of polymers.

INTRODUCTION

Polyoxetanes substituted in position 3, with repeating unit $-(\text{-CH}_2\text{-CR}_1\text{R}_2\text{-CH}_2\text{-O-})_n\text{-}$ being R_1 and R_2 hydrogen atoms or alkyl substituents, are a series of polymers where the influence of the pendent group on the thermal properties can be easily studied. For that purpose, we have studied the thermal transitions of several polyoxetanes, and the influence of the crystallization temperature on the melting behaviour and polymorphism of some of these polymers has been previously reported (1-4).

We are concerned here on the analysis of the effect of the substituent on 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 in liquid nitrogen 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

Figure 1 shows the thermograms corresponding to some selected polyoxetanes, quenched from the melt into liquid nitrogen to avoid crystallization of the sample. It is important to notice that the rate of crystallization is very different among polyoxetanes. Thus, unsubstituted polyoxetane (PTO) and the diethyl (PDEO), dipropyl (PDPO) and dibutyl (PDBO) derivatives are capable of crystallizing during the residence time in the calorimeter, while other polyoxetanes, like the dimethyl (PDMO), ethyl-methyl (PEMO) and tertbutyl (PTBO) 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 .

The corresponding values of T_g for the different polyoxetanes mentioned above are presented in Table I, showing a regular increase with the size of the linear substituents. A departure of this trend is observed for PDBO and may be assigned to the effect of internal plasticization found in other series of polymers, like poly(α -olefines) (6), poly(alkyl methacrylates) (7) or poly(vinyl alkyl ethers) (7,8). But all these series exhibit a continuous decrease of T_g beginning just on passing from the methyl to the

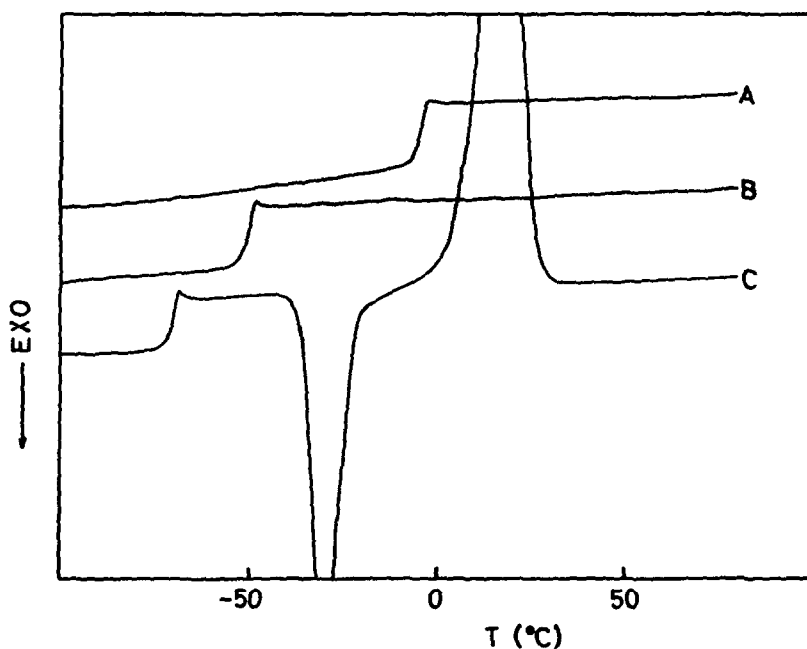


Fig. 1. DSC thermograms for several polyoxetanes quenched from the melt. A: PTBO; B: PDMO; C: PTO.

TABLE I

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
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(3,3-dipropyloxetane), PDPO (5)	-12	64.0	4.8
Poly(3,3-dibutyloxetane), PDBO (5)	-10	68.9	5.7
Poly(3-tertbutyloxetane), PTBO	-4	70.6	-

ethyl derivative. It is true, however, that poly(alkyl methacrylates) or poly(vinyl alkyl ethers) are different from polyoxetanes in that they carry a flexible group between the alkyl group and the backbone. Thus, poly(α -olefines) are structurally closer to polyoxetanes and in this series the increase in 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.

On the other hand, the T_g of PTBO is specially high, as usual for 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 I. The values of this parameter are rather constant and only PTO presents a CED substantially higher. This means that if the intermolecular interactions were dominant, PTO should exhibit the highest T_g of the series, and this is not the case.

On the other hand, the intramolecular factors can be correlated with the unperturbed dimensions as expressed by the characteristic ratio $|r^2|_0/nl^2$ (9). This parameter, as shown in Table II for several polyoxetanes, displays a smooth increase with the volume of the substituent, that is similar to the observed variation on T_g .

The main conclusion is, then, that the intramolecular factors, related to the restrictions for bond rotations, seems to be the dominant contribution in determining the glass transition temperature of polyoxetanes.

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