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Glass transition temperatures T_g of poly(tolyl methacrylates) and poly(di-xylenyl itaconates)

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Dedicated to Prof. Dragutin Fleš on the occasion of his 70th birthday

Summary

Glass transition temperatures of poly(phenyl methacrylates) and poly(diphenyl itaconats) with one and two methyl substituents in the phenyl ring were determined by DSC. Within the group of 17 investigated polymers it was attempted to correlate the T_g values obtained with the polymer repeat unit structure, considering steric effects and dipole/dipole interactions, inherent to various modes of (di)substitution.

Introduction

Investigating in this laboratory for a long time polymers derived from itaconic acid, i.e. 1-propene-2,3 dicarbonic acid, it was previously established that the introduction of one methyl group into each phenyl of the two monomer substituents, in the o-, m- or p- position, influences various polymer properties, such as dilute solution properties(1) or the thermal stability(2). Similar observations were recorded for poly(di-methyl phenyl methacrylates), i.e. poly (xylenyl methacrylates), regarding the overall rate constant k in the free radical polymerization of the corresponding monomers(3), with methyl groups in two of the five positions in each aryl ring, available for substitution,as well as for polymer solubility parameters(4). It was therefore thought reasonable to investigate the whole group of synthetised methyl and di-methyl substituted polymers, i.e. all poly(tolyl-) and poly(xylenyl methacrylates) and poly(di-tolyl-) and poly(di-xylenyl itaconates) regarding T_g and to try to estimate the influence of the steric hindrance and dipole/dipole interactions, respective the number and positions of $-CH_3$ of the aryl ring(s) in the polymer repeat unit.

While methacrylate monomers of this group yield polymers represented by the general formula $-(CH_2C(CH_3)R_1)-$, itaconate monomers yield polymers represented by $-(CH_2CR_1R_2)-$, where R_1 represents (.COO.Phenyl) and R_2 represents ($-CH_2COO$.Phenyl). Poly(methacrylates) thus contain one bulky R_1 substituent and a methyl group per monomer residue, however poly(itaconates) contain two bulky

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*To whom offprint requests should be sent substituents. The methyl groups introduced into the phenyl rings restrict the free rotation of the planar substituted phenyl around the O(ester)-C(aromatic) bond. In addition methyl groups crowding reduces the available conformations, restricting segmental motions. An additional stiffening contribution results from possible dipole/dipole interaction. Within every R substituent a strong dipole vector of μ= 1.85 D lies in the planar -COO- group(5). By substituting H with $-CH_3$ in the phenyl ring polarity is introduced, reflected in a weak dipole oriented in the direction of the C(aromatic)-C(methyl) bond, of the order of 0,4 D , as estimated from the polarity of the model substance toluene. Although the -COO- and -tolyl- or xylenyl-group are not coplanar, a dipole/dipole interaction in the substituent may reduce still further segmental mobility, influencing thus the glass transition temperature.

In the present investigation , polymers obtained from the following monomers were investigated :

Monomer	Polymer	Monomer	Polymer
Phenyl methacrylate	PFMA	Di-phenyl itaconate	PDFI
o-Tolyl methacrylate	PoTMA	Di-o-tolyl itaconate	PDoTI
m-Tolyl methacrylate	PmTMA	Di-o-tolyl itaconate	PDmTI
p-Tolyl methacrylate	PpTMA	Di-p-tolyl itaconate	PDpTI
2,3 Xylenyl methacrylate	P2,3XMA	Di-2,3 xylenyl itaconate	PD2,3XI
2,4 Xylenyl methacrylate	P2,4XMA	Di-2,4 xylenyl itaconate	PD2,4XI
2,5 Xylenyl methacrylate	P2,5XMA	Di-2,5 xylenyl itaconate	PD2,5XI
2,6 Xylenyl methacrylate	P2,6XMA	Di-2,6 xylenyl itaconate	PD2,6XI*
3,4 Xylenyl methacrylate	P3,4XMA	Di-3,4 xylenyl itaconate	PD3,4XI
3,5 Xylenyl methacrylate	P3,5XMA	Di-3,5 xylenyl itaconate	PD3,5XI

* PD2,6XI is so far unknown, the monomer does not polymerize.

Experimental

The synthesis and polymerization of all the monomers is described elsewhere(1,2,3,4). All polymers represent brittle non film forming white substances, easily crushed into powder. All polymer samples investigated had average molar masses between 50.000 and 500.000, except for P2,6XMA where the molar mass was lower.

The glass transition temperatures were determined on a Perkin-Elmer DSC-2 thermoanalyser, with samples of 10-15 mg in aluminium pans after ultimate drying of the samples for 4 hours i.vac. at 313 K. The scanning was performed in the temperature interval from 323-473 K at a heating rate of 20 K/min. The T_g was recorded as the middle of the shift of the base line.

Results and discussion

The first part of the results, referring to mono-substituted phenyl rings in the monomers, including also previously published and this time repeated values for PDFI(6), are presented in Table 1.

TABLE 1. Glass transition temperatures of poly' (tolyl methacrylates)and poly(-itaconates).

Poly(methacrylates)	T_g K	Poly(itaconates)	T_g K
PFMA	383	PDFI	403
PoTMA	382	PDoTI	403
PmTMA	380	PDmTI	381
PpTMA	403	PDpTI	409

The results presented indicate that in general T_g values of the di-tolyl poly(itaconates) are higher than the T_g values for corresponding poly(tolyl methacrylates), the differences ranging up to 20 K. In comparing the values for the two parent polymers PFMA and PDFI, with no additional steric hindrance from methyl-groups present, it is assumed that strong attraction forces between the planar phenyl rings, immobilizing in part the free rotation of the rings around the O(ester)-C(aromatic), are responsible for the values of T_g. Two phenyls per monomer residue in PDFI obviously have a stronger effect than one.

The results for the methyl-substituted polymers indicate that substitution affects the values of T_g. In absence of ring attractions, in the case of substitution in the o-position, the methyl-group seems to restrict strongly the free rotation of the phenyl ring. In this particular case a dipole/dipole interaction between the ester group dipole and the dipole introduced with the methyl group contributes further towards the reduced segmental mobility of the substituent groups as a whole. In the case of m- and p- substitution the dipole/dipole interactions are much weaker, the introduction of a methyl group in any of these two positions increases the bulkiness of the substituent but at the same time interferes with non substituted rings attractions, present in the parent polymers. T_g of both PmTMA and PDmTI are therefore lower. In both of cases the free volume is increased without creating strong steric hindrance : the m-tolyl group may ~~not~~ have an enlarged number of available conformations, increasing in this way the entropy of the system and loosening the structure in the glassy state.

A methyl-substituent in the p-position does not restrict the free rotation of the phenyl ring, because the substituent is located far away from the polymer chain backbone and the C(aromatic)-C(methyl) bond is on the axis of the O(ester)-C(aromatic) bond of the phenyl ring rotation. The volume excluded in rotation is smaller than in the case of o- or m-substitution and the net effect as a whole on steric hindrance is negligible. An explanation for the higher T_g values of PpTMA and PDpTI may result from the easiness of conformational changes of the p-tolyl group. Without any distorsions or with only minimum distorsions of the angle between the -COO-group and the phenyl group plains, a coplanar arrangement of phenyl groups is possible like in both parent polymers, leading to the establishment of attraction forces between the rings, contributing thus to a decrease of segmental motions and an increased glass transition temperature.

The explanation of the T_g values of the polymers with xylenyl groups is however more intricate, because of specific cumulative steric effects resulting from two methyl substituents and because of dipole/dipole interactions resulting from the -COO-group dipole and the combined two methyl group dipoles, diverging in dependence of the mode of substitution, but all lying in a single plain, for 60°, 120° or 180°. The glass transition temperatures of the two polymer groups are presented in Table 2.

TABLE 2. Glass transition temperatures of poly(xylenyl methacrylates) and poly(di-xylenyl itaconates)

Poly(methacrylates)	T_g K	Poly(itaconates)	T_g K
P2,6XMA	440	P2,6DXI	---
P2,3XMA	398	PD2,3XI	414
P2,4XMA	384	PD2,4XI	414
P3,5XMA	382	PD3,5XI	414
P3,4XMA	384	PD3,4XI	399
P2,5XMA	379	PD2,5XI	390

In discussing the T_g values of these two groups of polymers it should be mentioned first that substitution 2,6 (i.e. in both available o-positions) leads to very high steric hindrance. In P2,6XMA the phenyl rings seem to be highly restricted in rotation and irrespective of dipole/dipole interactions a very high T_g , higher for about 50 K compared to other polymers of this group, is detected. The high steric hindrance for this mode of substitution is reflected also in the lower molar masses observed for this polymer, indicating high chain transfer to the monomer in the free radical polymerization. With two 2,6 substituted phenyls in the corresponding itaconate monomer the steric hindrance is so high, that no polymer can be obtained, not even in copolymerization attempts, assuming the formation of charge-transfer complexes(7).

Practically no substantial difference is observed in T_g values between the 2,3 , 2,4 , 3,5 and 3,4 substitution for poly(methacrylates) and between the 2,3 , 2,4 and 3,5 substitution for poly(itaconates).There exists however a significant difference between the T_g levels of the two polymer groups,the values for the poly(itaconate) polymers with two bulky monomer repeat unit substituents are higher in all cases for about 25 K. The similarity of T_g values within each group must however be incidental, because of what is presented for single o-, m- and p-substitutions in the previous text, the effect of substitution on T_g is of different origin in each case. In the 2,3 and 2,4 substitution strong steric hindrance is caused by the o-substituent only,the m-substituent contributes to a loosening of the structure and to an increase of free volume, while the p-substituent has a similar effect, but without increasing the steric hindrance. The two dipole vectors of the 2,3 substitution diverging for 60° combine into a stronger resultant dipole vector, shifted for 30° in relation to the vector resulting from the o-substitution only. The resulting dipole/dipole interaction in the case of the 2,3 substitution additionally decreases the segmental mobility, leading to a high T_g. In the case of the 2,4 substitution, the steric hindrance results only from the substitution in position 2 , the combined resultant vector from the two methyl groups is weak and the steric effect of the substituent in the position 4 is negligible.However in this case increased ring attraction forces may balance the previously mentioned polar and steric effects.

In the case of the 3,5 and 3,4 substitution, the excluded volume from the rotation of the di-substituted phenyls is large, leading to increased free volume. The dipole/dipole interaction with the -COO- group dipole is insignificant and lower values should be expected. However in this case another factor is present, viz. the methyl group crowding, especially in PTMA , where repulsive forces between the two substituents of the ring and the $-CH_3$ group of the polymer backbone may limit the segmental motion.In poly(itaconates) no such methyl group linked to the polymer backbone is present. The lower value of T_g for P3,5-XI in relation to the preceding three polymers in the column is probably due to the combined effect of an increased free volume and methyl-group repulsions from the substituent pairs R_1/R_1 , R_2/R_2 and R_1/R_2.

The T_g values for the 2,5 substituted polymers support in general the assumption that dipole/dipole interaction is also responsible for the value of the glass transition temperature. In the case of the 2,5 substitution, the two dipoles introduced with each methyl substituent cancel each other because they diverge in direction for 180°, and consequently an interaction with the -COO- group dipole is absent. In this case dipole/dipole interactions are only possible between -COO- dipoles from neighbouring R substituents, but these must be weak and were not considered in this treatment. The strong hindrance of free rotation of the substituted phenyl rings, due to the substituent in position 2 , is conteracted by the increase in free volume resulting from substitution in the position 5. The net effect of the steric hindrance, the overall bulkiness of the substituents and the absence of dipole/dipole interactions result in a higher segmental mobility and T_g is thus lower than in all previously discussed polymers. The difference between the poly(methacrylates) and poly(itaconates) is however still present, but reduced to only 11 K.

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