

## Glass Transition of Polystyrene Model Molecules

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### Summary

The glass transition temperatures of 2,4-diphenylpentane, 2,4,6-triphenylheptane and 2,4,6,8-tetraphenylnonane are shown to follow the relation  $T_g = 325 - 2.64 \times 10^4 / M_n$  where  $M_n$  is the molecular weight. 2,4-diphenylpentane-2,4,6-triphenylheptane mixtures exhibit only one glass transition temperature which follow the relation  $T_g = (1 - \omega_2)T_{g1} + \omega_2 T_{g2}$  where  $\omega_2$  is the weight % of 2,4-diphenylpentane. The configurational structure of these polystyrene model molecules is shown to slightly influence the  $T_g$ 's values.

### Introduction

It is now well established that the glass transition temperature ( $T_g$ ) of amorphous polymers varies with the chain length. Recently COWIE (1975) has pointed out that the change of  $T_g$  versus the number of chain segments can be divided into three distinct regions : region I where the asymptotic value of  $T_g$  has been reached, region II where  $T_g$  becomes dependent on the chain length and region III which corresponds to oligomers and where  $T_g$  is even more chain length dependent. As far as polystyrene is concerned, the molecular weight boundary conditions are around  $\bar{M}_n = 21000$  and  $\bar{M}_n = 1500$  for regions I and II and regions II and III respectively. Low molecular weight materials are very often convenient models to get an insight into the influence of chain length and polymolecularity on  $T_g$  and a recent study (HATAKEYAMA and SERIZAWA, 1982) has shown that the glass transition temperatures of the oligomers having the same number of main chain segments were similar in spite of the difference in molecular weight.

The present experimental approach deals with the glass transition of very well defined polystyrene model molecules, i.e., 2,4-diphenylpentane, 2,4,6-triphenylheptane and 2,4,6,8-tetraphenylnonane.

### Experimental

The 2,4-diphenylpentane was prepared using the method of OVERBERGER and BONSIGNORE (1958) whereas 2,4,6-triphenylheptane and 2,4,6,8-tetraphenylnonane were prepared by a method developed in our laboratory (JASSE, 1978). The different stereoisomers of these compounds were separated by fast recycle gel permeation chromatography (JASSE et al., 1977). Polystyrene fractions were obtained from the Pressure Chemical Co. The glass transition temperatures were measured using a Du Pont 1090 thermal analyser. Heating rates of 15°K/min or 20°K/min were used and Tg was taken as the intersection of the base line with the extrapolated sloping portion of the curve, produced when a base line shift was observed during the transition.

### Results and discussion

Glass transition of PS model molecules. The glass transition temperatures measured for isopropylbenzene, s.butylbenzene, ethylbenzene, 2,4-diphenylpentane, 2,4,6-triphenylheptane, 2,4,6,8-tetraphenylnonane and different low molecular weight polystyrenes are given in table 1. Fig. 1 shows that a straight line holds

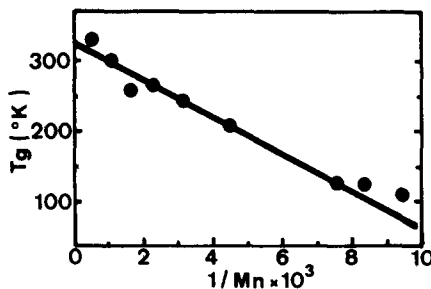


Fig. 1 - Relationship between  $T_g$  and  $1/M_n$ . Heating rate 15°K/min.

for  $T_g$  versus  $M_n^{-1}$  for all the studied model compounds but isopropylbenzene and ethylbenzene. This result suggests that s.butyl-

Table 1

Glass transition temperature of polystyrene model compounds and oligomers.

Compound	$M_n$	Tg/°K
Ethylbenzene	106	111
Isopropylbenzene	120	125
s.butylbenzene	134	127
2,4-diphenylpentane	224	208
2,4,6-triphenylheptane	328	243
2,4,6,8-tetraphenylnonane	432	263
Polystyrene	600	256
"	1000	302
"	2000	324

benzene is a more representative PS model compound than isopropylbenzene and ethylbenzene. On an other hand the Tg value obtained for  $\overline{M}_n = 600$  oligomer is lower than the expected value on account of the polydispersity of the sample (the molecular weight distribution is between 400 and 900).  $\overline{M}_n = 2000$  PS which belongs to region II does not follow any more the model molecules behavior.

Our data conform to the relation :

$$Tg = 325 - 2.64 \times 10^4 / \overline{M}_n$$

the coefficients of which are similar to the values obtained previously with PS oligomers (HATAKEYAMA and SERIZAWA, 1982).

Different mixtures of 2,4-diphenylpentane and 2,4,6-triphenylheptane exhibit, as expected, only one Tg falling on the tie line joining the Tg's of 2,4-diphenylpentane and 2,4,6-triphenylheptane (Fig. 2). The Tg of any mixture is then simply deduced from the equation :

$$Tg = (1 - \omega_2)Tg_1 + \omega_2 Tg_2$$

where  $\omega_2$  is the weight % of 2,4-diphenylpentane (component 2).

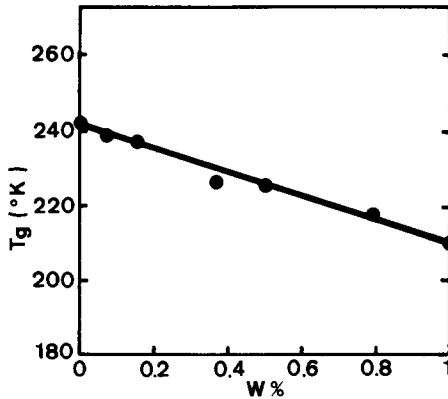


Fig. 2 - Glass transition temperature for blends of 2,4-diphenylpentane (1) and 2,4,6-triphenylheptane (2). The weight fraction of (1) is W. Heating rate 20°K/min.

Influence of the configurational structure. Although several authors first considered that PS glass transition was independent of tacticity (NEWMAN and COX, 1960, KARASZ et al., 1965, KARASZ and MACKNIGHT, 1968), it is now well established that the Tg of quenched isotactic PS is about 10°K lower than atactic PS glass transition (ALI and SHELDON, 1970, CURRIE and DOLE, 1969). One can expect to detect a similar effect in the stereoisomers of PS model molecules. The results, given in table 2, suggest some comments. The first one is that the Tg's are actually dependent on the configurational structure. However the Tg of meso 2,4-diphenylpentane is lower than the racemic one while the Tg of the isotactic isomer is higher than the syndiotactic one in 2,4,6-triphenylheptane. Such a behavior cannot be clearly interpreted on the basis of the conformational energies or activation enthalpies previously calculated and measured for these molecules (FROELICH et al. 1976, 1978). As far as 2,4,6,8-tetraphenylnonane is concerned, one can also notice an influence of the tacticity on Tg's. These results clearly indicates a slight influence of configuration on glass transition but do not allow to explain the different behavior between atactic and isotactic polystyrene which certainly follows from specific polymeric properties.

Table 2

Influence of configuration on glass transition of PS model molecules. Heating rate 15°/min.

Molecule	Configuration*	T <sub>g</sub> /°K
2,4-diphenylpentane	r	210
	m	207
2,4,6-triphenylheptane	rr	240
	rm	245
	mm	247
2,4,6,8-tetraphenylnonane**	rrr	260
	rnr	260
	rmm	260
	mrm	263
	mrr	263
	rnr	

\* r : racemic diad; m : meso diad

\*\* The isotactic isomer was not studied on account of the lack of enough product.

#### References

- ALI, M.S. and SHELDON, R.P.: J. Appl. Polym. Sci. 14, 2619 (1970)
- COWIE, J.M.G.: Europ. Polym. J. 11, 297 (1975)
- CURRIE, J.A. and DOLE, M.: J. Phys. Chem. 73, 3384 (1969)
- FROELICH, B., NOEL, C., JASSE, B. and MONNERIE, L.: Chem. Phys. Letter 44, 159 (1976)
- FROELICH, B., JASSE, B., NOEL, C. and MONNERIE, L.: J. Chem. Soc. Faraday Trans. II 74, 445 (1978)
- HATAKEYAMA, T. and SERIZAWA, M.: Polym. J. 14, 51 (1982)
- JASSE, B., LAUPRETRE, F. and MONNERIE, L.: Makromol. Chem. 178, 1987 (1977)
- JASSE, B.: Bull. Soc. Chim. Fr. II, 535 (1978)

KARASZ, F.E., BAIR, H.E. and O'REILLY, J.M.: J. Phys. Chem. 63, 2657 (1965)

KARASZ, F.E. and MACKNIGHT, W.J.: Macromolecules 1, 537 (1968)

NEWMAN, S. and COX, W.P.: J. Polym. Sci. 46, 29 (1960)

OVERBERGER, C.G. and BONSIGNORE, P.V.: J. Am. Chem. Soc. 80, 5427 (1958)

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