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Characterization of a crystalline organosilicic polymer: Poly[1-(dimethyl)silyl, 4-(dimethylethylene)silyl benzene]

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SUMMARY

The present note deals with the characterization of a serie of telechelic organosilicic polymers (Mn, Tg, Tm, ΔHm). These crystallizable polymers can been used as precursor molecules in the synthesis of multiblock copolymers, in association with amorphous blocks.

INTRODUCTION

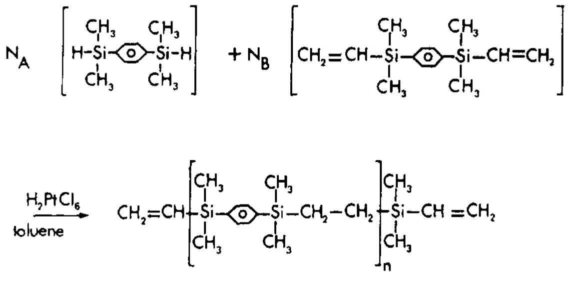
To investigate the gelation behaviour of multiblock copolymers in which crystalline "hard" blocks are associated with amorphous "soft" blocks (1), we have been interested in materials made up with crystallizable organosilicic blocks and flexible poly dimethyl siloxane blocks (PDMS).

In the present note we will report a study of the physical characteristics of the crystallizable telechelic polymer used as a "hard" block : poly [1-(dimethyl)silyl,4-(dimethylethylene)silyl benzene]. The latter will be designated as COSP (crystallizable organosilicic polymer) throughout the text.

To carry out the present investigation, we have synthesized a serie of organosilicic polymer samples with different average molecular weights.

SYNTHESIS

The COSP samples have been prepared according to a synthesis perfected by Ch. Prud'homme (2,3), which is based on the hydrosilylation reaction (addition reaction between a silane function and a carbon-carbon double-bond). The polymers are obtained by reacting bis 1,4-(dimethylsilyl)benzene (compound A) and bis 1,4-(dimethylvinylsilyl) benzene (compound B) as shown by the following reaction scheme :



COSP

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As with polycondensation reaction, the average molecular weight of the polymer formed is fixed by the stoichiometric ratio

$$r = \frac{N_A}{N_B}$$

Depending on the excess of molecules N_A or N_B used, the telechelic macromolecules obtained can be fitted either with silane or with silvinylic groups at both chain-ends. Polymers with end-standing silvinylic functions were used in the present study. The synthesis was carried out in toluene at 90°C in the presence of chloroplatinic acid as a catalyst.

CHARACTERIZATION

Number Average Molecular Weights

Since the organosilicic polymers described above crystallize quite rapidly at room temperature, even in dilute solution, a characterization by gel permeation chromatography is not possible. Besides, the experimental conditions required for light scattering measurements represent also major difficulties. Therefore, we have determined the number average molecular weights of our samples by tonometry (vapour pressure osmometry) using a KNAUER instrument. The measurements were performed at 90°C in toluene. The accuracy of this technique is good in the low molecular weight range ($\bar{M} \leqslant 10\ 000$).

Table 1

Ref	r	$\bar{M}n$ (th)	$\bar{M}n$ exp	$\overline{DP}n$	p
COSP	1.0				
COSP 8	0.946	8000	7800	35.3	0.999
COSP 6	0.929	6000	5400	24.5	0.998
COSP 4.5	0.907	4500	3900	17.5	0.992
COSP 2	0.802	2000	2100	9.4	1
COSP 1	0.639	1000	1200	5.3	1

On Table 1 are gathered the characteristics of the samples. The measured values of the molecular weights ($\bar{M}n$ exp) are rather close to those theoretical expected ($\bar{M}n$ th). Moreover the extent of the hydrosilylation reaction is very high.

Thermodynamic Parameters

Glass transition temperatures Tg, melting temperatures Tm and melting enthalpy ΔHm have been determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC 4 instrument. Approximately 5mg were placed into a sample pan. The experiments were calibrated with indium.

On Figure 1 is represented a typical DSC trace obtained by heating at 20°C/mn a sample that had been molten beforehand and then quenched at - 18°C. Once heated above its glass transition temperature, the polymer undergoes a rapid crystallization which appears on the DSC diagram as an exotherm (Tc).

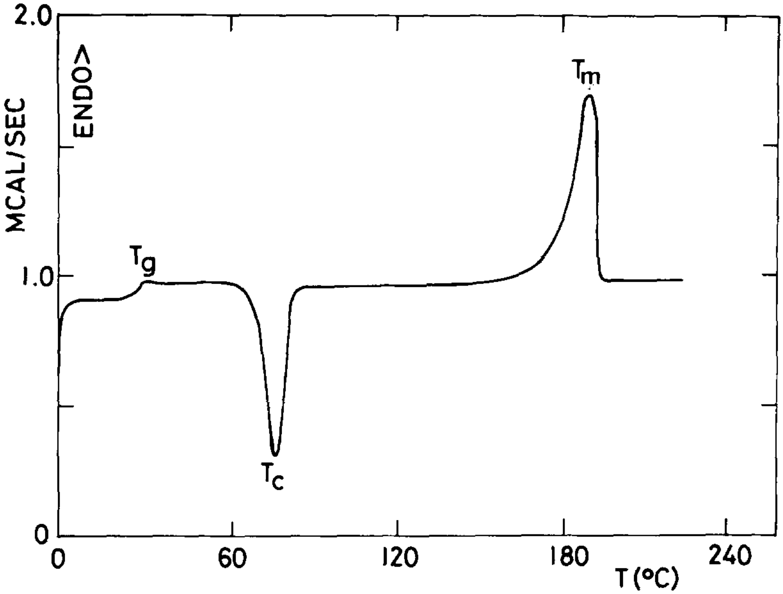

Figure 1. DSC trace of COSP 8 at a heating rate of 20°C/mn after quenching from 210°C to - 18°C.

Table 2

Ref	$\bar{M}n$	Tg (°C)	Tm (°C)	ΔHm(cal/g)
COSP 8	7800	24	189	13.3
COSP 6	5900	22	188	12.1
COSP 4.5	3900	19	186	11.8
COSP 2	2100	12	181	11.7
COSP 1	1170	- 2	165	10.8

All DSC data obtained are reported in Table 2. In principle, the glass transition temperature is molecular weight dependent according to the following law (4) :

$$Tg = Tg^{\infty} - \frac{K}{M_n}$$

where K is a constant and Tg the glass transition temperature of the infinite molecular weight polymer. Figure 2, where the Tg-values are plotted versus $1/\bar{M}n$, shows that this is also the case here : the experimental points fit a straight line with a slope

$K = 3.5 \times 10^4$ and which extrapolates to $Tg = 28°C \pm 0.5°C$

The melting temperature Tm does not vary drastically with molecular weight and follow the usual pattern.

The melting enthalpies ΔHm have been determined on samples that were first molten at 210°C and then slowly cooled at a rate

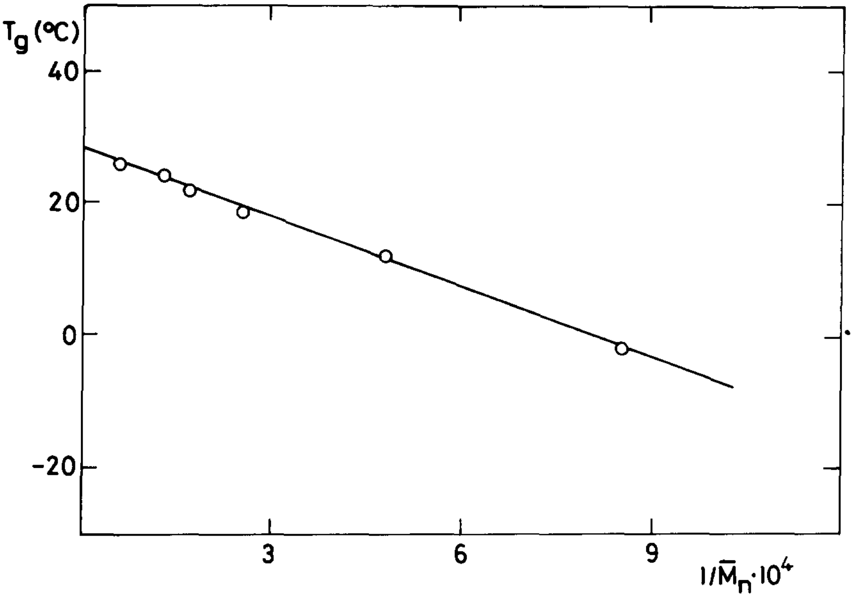

Figure 2. Tg vs 1/M̄n.

of 2°C/mn. The use of lower cooling rates did not lead to an increase of the values measured for ΔHm. As expected the melting enthalpy increases with molecular weight. The values reported here probably correspond to fully crystallized samples and may be used to measure a degree of crystallinity.

CONCLUSION

To conclude, the organosilicic polymer investigated here possesses some interesting features :
(i) it can be obtained in the amorphous state
(ii) it crystallizes however, very rapidly once heated above its glass transition temperature
(iii) it exhibits rather high melting points.

According to the above characteristics, this polymer can be considered as an excellent candidate to be used as a crystalline block in a (crystalline-amorphous) multiblock copolymer to study physical gelation.

REFERENCES

1. X.W. He, J. Herz and J.M. Guenet, to be published.
2. C. Prud'homme, Thesis, Strasbourg (1980).
3. M. Bargain and C. Prud'homme, Ger. Offen. **2**, 901-514 (1979); Chem. Abst. **91**, 141-946d (1979).
4. P.J. Flory in "Principle of Polymer Chemistry", Ithaca, Cornell University (1953).

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