Synthesis and characterization of multiblock copolymers containing poly(dimethyl siloxane) blocks

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Multiblock copolymers of polystyrene and poly(dimethyl siloxane) were obtained by a hydrosilylation reaction between **a,w** dihydrogeno poly(dimethyl siloxane) and **a,w**-di(vinyl silane) polystyrene. Under well chosen experimental conditions the polycondensation is free of site reactions and the macromolecules formed are linear with up to 10 blocks, which corresponds to reaction of 90% of the functions initially present. The block copolymers obtained have been characterized by g.p.c. viscosimetry and light scattering.

INTRODUCTION

Poly(dimethyl siloxanes) (PDMS) exhibit some interesting features such as: high surface tension, large permeability to gases, high hydrophobicity, low chemical reactivity and good biocompatibility; the glass transition temperature of PDMS is very low ($< -120°C$) and the chain flexibility at room temperature is very high.

However, many potential applications of this polymer are hindered by its poor mechanical properties: above T_g, PDMS behaves as a viscous liquid unless it is of extremely high molecular weight, or even crosslinked.

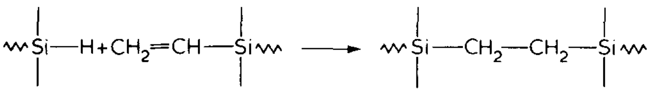
To improve the mechanical behaviour of this polymer, while keeping its other characteristic properties, it was attempted to synthesize block copolymers in which PDMS blocks would be associated with polyvinylic blocks, chosen preferably among those exhibiting high glass transition temperatures. These materials should exhibit the properties of thermoplastic elastomers, with possible biomedical applications, provided the biocompatibility of PDMS is retained.

To synthesize such block copolymers, it was attempted to 'polycondensate' α,ω-functional PDMS chains with α,ω-functional polyvinylic chains, the functions carried at chain end by the two precursor polymers being able to react in a close-to-quantitative manner.

This basic principle has been used previously. Marsiat[1] and Greber[2] reacted 'living' α,ω-dicarbanionic α-methylstyrene oligomers with poly(dimethyl siloxane) blocks carrying end-standing [$\Rightarrow$Si–Cl] functions. However in this case side reactions are likely to occur, owing to the high nucleophilicity of the α-methylstyryl carbanions.

Matzner *et al.*[3] have carried out polycondensation reactions between α,ω-dihydroxy polycarbonate chains and PDMS chains fitted at both ends with dimethylaminosilane functions. When the same reaction is applied to hydroxy terminated poly(α-methylstyrenes)[4] the results are not satisfactory.

In the present work hydrosilylation is applied to 'polycondensate' PDMS chains carrying at both chain ends silane ($\Rightarrow$Si–H) functions, the polymers exhibiting end-standing vinylsilane functions. The addition reaction:



$$\sim\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-H+CH_2{=}CH-}\overset{|}{\underset{|}{\mathrm{Si}}}\sim \longrightarrow \sim\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{-CH_2-CH_2-}\overset{|}{\underset{|}{\mathrm{Si}}}\sim$$

requires chloroplatinic acid (H_2PtCl_6, $6H_2O$) or similar compounds, as catalysts.

In previous experiments polyvinylics with end-standing allylic functions were used instead of vinylsilane. However the hydrosilylation yields are better when vinylsilane groups are used as the antagonist functions[6].

In a preceding paper[5] we showed that polystyrene chains (or related polymers) can be fitted in a quantitative manner with vinylsilane functions at chain ends. We shall describe now the synthesis of multiblock copolymers, according to the above principle, and the characterization of the obtained polymer species, by g.p.c. and by light scattering. Polystyrene, poly(α-methylstyrene), poly(vinyl mesitylene), poly(p-trimethylsilylstyrene), and poly(p-trimethylsilyl-α-methylstyrene) were chosen as the amorphous vitrous blocks of high T_g to be linked with the elastomeric PDMS blocks.

EXPERIMENTAL

α,ω-difunctional polymers

PDMS — A series of PDMS samples, the chains of which are fitted at both ends with silane functions, were obtained from Rhone–Poulenc, Division Chimie Fine. They cover a molecular weight range from 1700 to 25 000. Their molecular weight distribution is characterized by a M_w/M_n ratio of the order of 1.5.

Polystyrene and substituted polystyrenes. The synthesis of α,ω-divinylsilane polymers has been described in a previous paper[6]. Anionic 'living' polymerization of the monomers is carried out in THF, at low temperature, using an efficient bifunctional initiator (potassium salt of

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α-methylstyrene 'tetramer'). Thereafter chlorodimethylvinylsilane is reacted at low temperature (−90°C) with the carbanionic sites to yield the end-standing vinylsilane functions in close-to-quantitative yields.

Synthesis of multiblock copolymers

The 'polycondensation' reaction is carried out in a tight reactor, fitted with efficient stirring, under a slight argon overpressure. Stoichiometric amounts of the two α,ω-difunctional polymers (PS and PDMS) are dissolved in toluene, at concentrations ranging up to 50% and introduced into the reactor. The mixture is heated to 95°C and then a known volume of a 1% chloroplatinic acid solution in isopropanol is added. The mole ratio of catalyst to polymer was chosen 5×10^{-4}.

The reaction mixture is heterogeneous at the start. After a given time (dependent upon the reaction conditions) it becomes homogeneous and the reaction speeds up. After several hours at 95°C, when the yield is considered to be quantitative, the reaction medium is diluted to ~10% by weight, and cooled to room temperature. The copolymer is precipitated from methanol, filtered, washed and dried.

The copolymers are soluble in benzene, toluene and THF. They precipitate as fibrous materials exhibiting elastic properties.

Characterization of the block copolymers

(a) gel permeation chromatography

Our samples are characterized first by g.p.c. using a Waters apparatus fitted with a set of 5 columns. THF is the elution solvent (flow rate, 1 ml min^{-1}) and detection is performed by differential refractometry. The calibration curve is constructed using the elution volumes of a set of narrow molecular weight polystyrene samples.

In THF the refractive index increment of PDMS is close to zero. This fact was taken into consideration for the determination of the molecular weights of the samples studied: The values of $\bar{M}_n$ and of $\bar{M}_w$ are calculated from the g.p.c. curves, taking into account the calculated composition of the block copolymers.

A small shoulder is observed in many instances, the elution volume of which corresponds to that of the precursor vinyl polymer. Because the refractive index increment of this polymer is higher than that of the block copolymer, a correction is necessary to keep the ordinate proportional to the weight of polymer eluted.

We did not make use of the 'universal calibration' to characterize our samples. Also, an error is involved when the PS calibration curve is used to correlate elution volumes and molecular weights for samples containing another species.

From the number average molecular weight of the block copolymer and those of the two corresponding functional 'precursor' polymers it is easy to calculate the degree of polycondensation attained ($\overline{DP}_n$) and the probability p for any given end-standing function to be involved in the reaction.

(b) Light scattering

The light scattering measurements on our samples are carried out in THF using a FICA instrument. The refraction index increments are either calculated from the d*n*/d*c* of the corresponding homopolymers, taking into account the composition of the samples, or measured using a Brice Phoenix differential refractometer. The good agreement between the experimental values and those calculated confirms that the average composition of the samples is precisely that of the reaction mixture from which it originates.

When applied to copolymers, light scattering yields 'apparent' values. However when the fluctuations in composition remain small within a sample this apparent value comes very close to the real value. This is the case of our copolymers, provided the number of blocks is at least equal to 4.

(c) Limiting viscosity number $[\eta]$

The intrinsic viscosities of our samples are measured in THF solution, at 25°C, using an automatic capillary viscometer.

However, owing to the intramolecular interactions characteristic of block copolymers, the accuracy is lowered.

(d) ^{1}H-n.m.r.

The composition of our samples can be determined by proton n.m.r. from the ratio of aromatic protons (originating from the polystyrene blocks) to the number of methyl protons of the PDMS blocks. The experiments are carried out in CCl_4 using a Hitachi Perkin Elmer 60 MHz spectrometer. However the low accuracy of the integral n.m.r. curves allows only a qualitative check of the composition of our samples.

RESULTS AND DISCUSSION

The chief characteristics of the functional precursors that have been submitted to 'polycondensation' by means of hydrosilylation reaction are indicated in *Table* 1. In no case was the PDMS content of the multiblock copolymer lower than 52% by weight, owing to the molecular weights of the precursors that have been brought to reaction.

Table 2 displays the main results of the experiments carried out, namely the number and weight average molecular weights of the block copolymers formed, their

Table 1 Number-averages of the molecular weights of the two precursor polymers. $\bar{M}_{n,R}$, vitrous blocks; $\bar{M}_{n,S}$, PDMS blocks; PS, polystyrene; PMS, poly(α-methylstyrene); PVM, poly(vinyl mesitylene); PSS, poly(*p*-trimethylsilylstyrene); PSMS, poly(*p*-trimethylsilyl-α-methylstyrene)

Block copolymers	Vitrous blocks	$\bar{M}_{n,R}$ g mol^{-1}	$\bar{M}_{n,S}$ g mol^{-1}	% PDMS
COP 25	PVM	3800	9300	71
26	"	3800	6400	63
27	"	3800	4150	52
31	PMS	4500	6400	59
32	"	4500	9300	67
33	"	4500	13250	75
34	"	4500	17100	79
36	PVM	6100	9300	60
37	"	6100	13250	68
38	"	6100	17100	74
39	PMS	5400	6400	54
40	"	5400	9300	63
41	PS	10500	13250	56
42	"	10500	17100	62
43	PMS	9400	13250	58
46	PSS	10500	17100	62
47	PSMS	8900	17100	66
48	"	13000	17100	57
49	"	9200	17100	65
51	"	9200	25000	73

Table 2 Experimental data concerning the block copolymers. $\bar{M}_{n,\mathrm{g.p.c.}}$: number averages of the molecular weight calculated from the g.p.c. diagrams. $\bar{M}_{w,\mathrm{g.p.c.}}$: weight averages of the molecular weight calculated from the g.p.c. diagrams. $\bar{M}_{w,\mathrm{LS}}$: weight averages of the molecular weight calculated from the light scattering data. $\overline{DP}_n$..: average degree of polycondensation calculated from the g.p.c. values. p . . . . : probability for any end-standing function of the precusor polymers to react. $[\eta]_{\mathrm{THF}}$: limiting viscosity numbers in THF solution at 25°C. t_H. . . : approximate duration until the medium becomes homogeneous

Block copolymer	$\bar{M}_{n,\mathrm{g.p.c.}}$ (g mol^{-1} 10^{-3})	$\bar{M}_{w,\mathrm{g.p.c.}}$ (g mol^{-1} 10^{-3})	$\bar{M}_{w,\mathrm{LS}}$ (g mol^{-1} 10^{-3})	$\overline{DP}_n$	P	$[\eta]$ THF (cm^3 g^{-1})	t_H (mn)
COP 25	44	110	–	6.7	0.85	–	<1
26	42	120	–	8.2	0.88	–	<1
27	28	70	–	7.0	0.86	–	<1
31	27	65	41	5.0	0.80	–	<1
32	27.5	72	68	4.0	0.75	–	1
33	35	89	70	4.0	0.75	–	2
34	37.5	94	90	3.5	0.71	–	8
36	54	140	190	7.1	0.86	~60	5
37	65	175	310	5.6	0.82	~70	8
38	76.5	270	–	6.6	0.85	~70	~15
39	37	97	93	6.3	0.84	~40	~15
40	38.5	100	85	5.2	0.81	–	~50
41	49.5	300	600	4.2	0.76	–	>360
42	43	170	800	3.1	0.68	–	>360
43	56	150	150	4.9	0.80	–	~360
46	34	90	110	2.5	0.60	–	~10
47	120	260	300	9.2	0.89	–	<1
48	77	220	250	5.1	0.80	–	~180
49	93	210	460	7.1	0.86	–	~15
51	110	250	190	6.4	0.84	–	~100

intrinsic viscosity, the calculated 'degree of polycondensation' and the probability for a given function to have undergone reaction. The time after which the reaction medium has become homogeneous is also indicated.

Homogenization time — considerations about the reaction process

Owing to the drastic incompatibility between PDMS and vinyl polymers[7], and to the high concentrations required for the reaction to proceed, the reaction medium is heterogeneous at the start. However, after a given time (dependent upon the reaction conditions chosen and upon the molecular weights of the precursor polymers) the mixture becomes homogeneous, since the block copolymer formed in the early stages of the reaction acts as a compatibilizer for the remaining homopolymers. The time required to attain homogeneity, t_H, increases sharply as the molecular weights of the precursors increase (*Table* 2). We have characterized the composition of the initially formed two-phase system using ^{1}H-n.m.r. A turbid mixture of PDMS and polystyrene in toluene was allowed to settle at 90°C over several hours, Phase separation is very slow, but eventually two layers are formed, corresponding to two separate phases φ_1 and φ_2. N.m.r. analysis shows that the upper layer φ_1 contains almost all of the PDMS precursor chains. The lower layer φ_2 contains all of the PS and a small fraction of the PDMS. The amount of PDMS found in the phase φ_2 decreases as the molecular weights of either precursor increase.

In an earlier investigation[6] it has been shown that the hydrosilylation reaction requires elevated concentrations, and that the yields attained increase as the overall concentration increases. In the present case it can be assumed that either the reaction starts at the interphase, or it first involves the small amount of PDMS present in φ_2, together with the PS. An argument in favour of the latter assumption is the fact that t_H increases as the amount of PDMS in φ_2 decreases, i.e. when the PDMS molecular weight increases.

When polystyrene is replaced by poly(*p*-trimethylsilylstyrene) (or by poly(*p*-trimethylsilyl-α-methylstyrene)) in a 'polycondensation' experiment with PDMS the time t_H to reach homogeneity is found to be shorter, the molecular weights and concentrations remaining the same.

It can thus be reasonably assumed that the reaction starts in the φ_2 phase containing the vinyl polymer together with some PDMS, and that, once some block copolymer is formed, it acts as a compatibilizing agent; when the reaction medium has become homogeneous, the reaction speeds up. However, the assumption of a reaction at the interphase cannot be rejected entirely at present.

Degree of polycondensation

Under ideal conditions of exact stoichiometry and absence of any side reaction, the reaction can be expected to yield high degrees of polycondensation. In fact the results obtained can be considered satisfactory if account is taken of the very high viscosity of the reaction medium, a factor strongly decreasing the rate of reaction between polymer molecules. Experimental number average *DP*s range from 3 to 9 (which means that a copolymer molecule contains 3–9 blocks) and the corresponding conversion degrees *p*, calculated from the *DP*s range from 0.7 to 0.9.

In two cases (41 and 42) the reaction mixture was still inhomogeneous when the polycondensation was stopped. This accounts for the rather low polycondensation degrees attained, and possibly also for the large discrepancies between the weight average molecular weights obtained from g.p.c. and from light scattering measurements. The latter values are too high. This can be explained by phase separation effects, but it could also originate from side reactions that would introduce some crosslinking (especially for COP 42, in which additional catalyst had been introduced to try to speed up the reaction).

In all other cases the agreement between light scattering and g.p.c. results are satisfactory, if account is taken of the accuracy of the measurements for the systems investi-

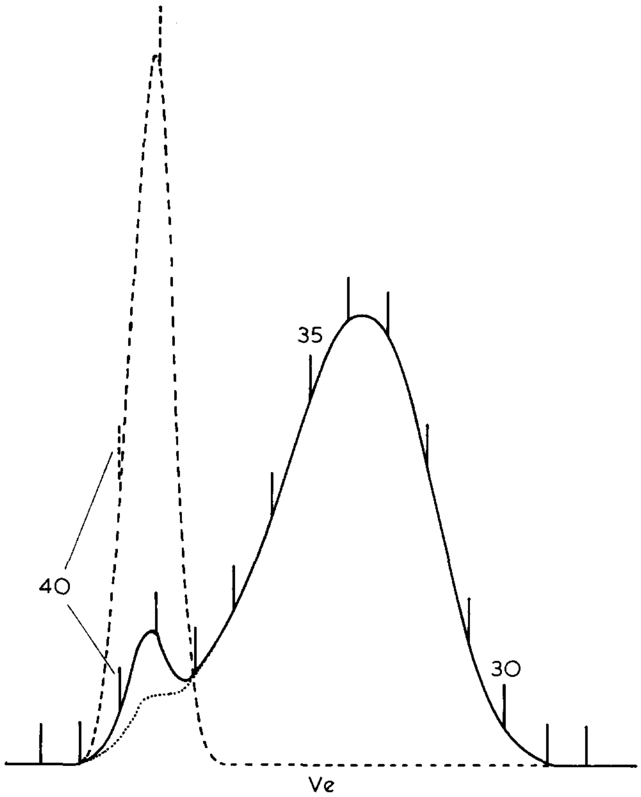

Figure 1 G.p.c. diagram of COP 43. (———), experimental curve copolymer; (— — — —), experimental curve homopolymer (P MS); (· · · · ·), curve corrected to account for the difference in d*n*/d*c* for homo- and block copolymer

gated, and the restrictions discussed in the experimental part.

Polydispersity of the samples obtained

If a polycondensation reaction is carried out under conditions of sharp stoichiometry, to a conversion *p*, the ratio of the weight average degree of polycondensation to its number average is given by:

$$\frac{\overline{DP}_w}{\overline{DP}_n} = 1 + p$$

and as *p* tends to unity the polydispersity ratio should come closer to 2. In the present case, polycondensation is carried out between polymer species each of which exhibits a given polydispersity. The PDMS precursors have polydispersity ratios of the order of 1.5, and the anionically obtained polystyrenes (and derivatives) exhibit polydispersity indices of the order of 1.1. A g.p.c. trace of one of these functional precursors is shown in *Figure* 1. However, provided the average number of blocks of the 'polycondensate' is >4, the contribution of the molecular weight distribution of the precursor polymers to the overall polydispersity of the sample can be considered negligible.

The polydispersity ratios determined experimentally from the g.p.c. traces of our multiblock copolymers range from 2.2 to 4, however in most cases they are close to 2.5. As possible deviations from exact stoichiometry cannot account for a broadening of the molecular weight distribution, and since we have shown that the precursor polydispersities do not contribute significantly, we have to assume that the increased polydispersity originates either from a side reaction or from an artifact in the course of the g.p.c. elution.

CONCLUSION

Hydrosilylation reaction between α,ω-dihydrogeno poly(dimethyl siloxanes) and α,ω-divinylsilane polystyrene derivatives yields polycondensation resulting in multiblock copolymers. When carried out under well chosen experimental conditions, this reaction is essentially free of side reactions and the macromolecules obtained are linear, with up to 10 blocks, which corresponds to a consumption of about 90% of all functions initially present in the reaction mixture. Similar results have been published recently by Marechal[8] who applied hydrosilylation reactions to establish links between PDMS blocks and polyesters fitted at chain ends with allylic functions.

The block copolymers that were obtained are soluble in various solvents and have been characterized by the usual techniques such as g.p.c., viscosimetry and light scattering. An investigation of the thermomechanical behaviour of these polymers is in progress and will be published in a near future.

The same method can be used to synthesize triblock-copolymers of a central PDMS block surrounded by two vitrous polyvinylic blocks. In that case the polyvinylic precursor has to be fitted with a functional vinylsilane group at one chain end only.

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