Combination of polymer ions. Formation of copolymer containing polytetrahydrofuran and poly(dimethylsiloxane) blocks

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(Received 9 *November* 1981*)*

The polymerization of tetrahydrofuran initiated by a silenium (silyl-enium) initiator with perchlorate counterions proceeds without transfer and termination i.e. *via* a 'living mechanism. However, the degree of polymerization of the product is lower. This was explained by the ability of the ester form of an active centre to form macrocycles. The combination of living dianionic poly(dimethylsiloxane) with silenium dicationic initiator increases the molecular weight of the initial poly(dimethylsiloxane) by an order of magnitude. The A(BA)$_n$B type block copolymer was prepared from dianionic poly(dimethylsiloxane) and dicationic polytetrahydrofuran by an analogous reaction. The $-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\mathrm{CH_2}-$ bond is relatively stable towards hydrolysis.

Keywords Combination; macroions; poly(dimethylsiloxane); polytetrahydrofuran; block copolymer; macrocycles

INTRODUCTION

We have already pointed out[1] that the neutralization of growing centres through combination takes place upon mixing of anionic and cationic poly(dimethylsiloxane). Hence, this reaction can be utilized in the preparation of block copolymers. Particular examples have been reported by several authors[2–5] who have studied the coupling of 'living' polystyrene ends with polytetrahydrofuran (pTHF).

Block copolymers $\sim$bTHF–bD$\sim$(D = –Si(CH$_3$)$_2$–O–) have already been employed practically[6]. A direct combination of macroions might have certain advantages when compared with synthetic modes making use of end-group combination[6].

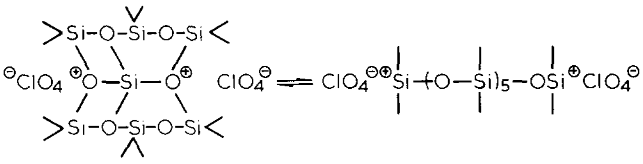
Block copolymers are efficient interfacially active agents. The isolation of combination products using conventional extraction or chromatographic procedures is not satisfactory. There is always a certain overlap of effects based on the molecular weight and macromolecule composition. Frequently an emulsion of a homopolymer (and/or copolymer containing short blocks of soluble composition. Frequently an 'emulsion' of a homopolymer the extraction. This difficulty may be avoided by selecting suitable components to study the combination. Living poly(dimethylsiloxane) may be both cationic and anionic so that the homopolymer formed through combination may be analysed reliably using simple analytical methods.

EXPERIMENTAL

Solvents of analytical grade were used without further purification. Octamethylcyclotetrasiloxane (D$_4$) was stored *in vacuo* under continuous stirring in the presence of sodium. It was freshly distilled prior to each run. Tetrahydrofuran, analytical grade, was always distilled at least twice from a green solution of sodium naphthalene. Before drying the purity of both monomers was checked by g.l.c. The concentration of impurities, which were not of polar character, did not exceed 0.1%.

Initiators

Sodium naphthalene was prepared by a procedure described elsewhere[7]. The synthesis of silenium dication was effected by a two-step hydrolysis of Cl$_2$Si(CH$_3$)$_2$ with aqueous HClO$_4$, the condensation equilibrium being shifted in high vacuum. The obtained dication



contained less than 2 mol% of $>$SiOH groups with regard to –Si$^+$ClO$_4^-$.[8] The initiator was dissolved in benzene to obtain a concentration of *ca* 0.4 mol dm^{-3}. Initiators were transferred to the reactors by a syringe under a stream of dry nitrogen (H$_2$O content < 2 ppm).

Apparatus and procedure

The combination of silicon containing chains. The reaction vessel, represented by part 3 in *Figure 1* (left hand side of the doubled reactor), was attached to a vacuum line (10^{-3}–10^{-4} Pa) and pumped down for 8 h while blowing warm (480 K) air occasionally onto the outer surface. THF was distilled from a solution containing a very low concentration of green sodium naphthalene into the dried reaction vessel (12.2 cm^3, 0.150 mol); to this 35.4 cm^3 (0.118 mol) of octamethylcyclotetrasiloxane was distilled. When a temperature of 298.1 K was established the solution of sodium naphthalene in THF was added by

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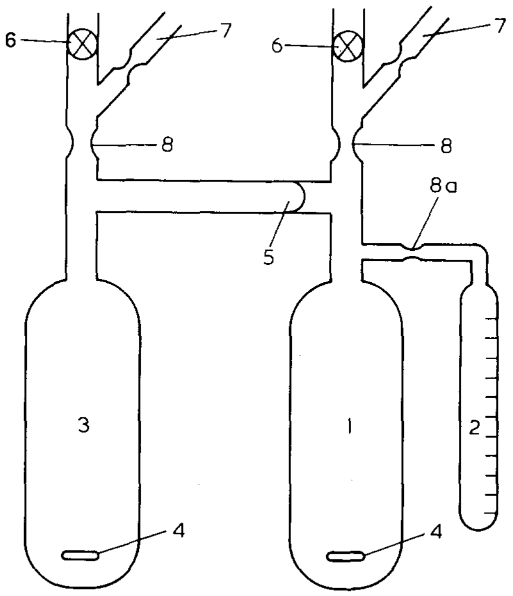

Figure 1 Reactor for combination of pD with pTHF (1) polymerization vessel for D_4; (2) calibrated bulb for reference sample; (3) polymerization vessel for THF; (4) stirrers; (5) break seal; (6) two-way stopcocks; (7) attachments to line; (8) seal off points

means of a hypodermic syringe while flushing the reactor with dry nitrogen. The concentration of the initiator was selected to be 7.3 mmol dm^{-3}. The solution was degassed and left to polymerize at 298.1 K. After 50 h the solution became red. After 821 h polymerization the reactor was cooled down to 263.1 K and filled with dry N_2. Then a reference sample was taken by a syringe. Almost simultaneously the poly(dimethylsiloxane) reference sample was injected into the excess of methanol and the silenium dication was added to dianionic red solution in the reactor in such an amount that the concentrations of anions and cations were equal.

The solution in the reaction vessel became very viscous and lost its colour upon stirring. It was left for 24 h and then transferred into an excess of methanol. Both the reference sample and product were washed with methanol several times, dried to constant weight and analysed.

THF polymerization. The dilatometer shown in *Figure 2* was attached to vacuum ($10^{-3}-10^{-4}$ Pa) and occasionally warmed up by blowing in hot air. The silenium initiator in benzene was then added while flushing the apparatus with dry nitrogen. After degassing and removing benzene the THF was distilled into the dilatometer. Then the reactor was sealed off, thermostatically controlled to a selected temperature and the contraction was measured as a function of time. The reactor was then opened and a 2% methanolic solution of ammonium hydroxide was added to the pTHF solution. The polymer was washed with pure MeOH 4–5 times, dried to constant weight and analysed.

Combination of poly(dimethylsiloxane) with pTHF. The combination of dianionic poly(dimethylsiloxane) with dicationic pTHF was carried out in the apparatus shown in *Figure 1*, where two reaction vessels are connected, the break-seal separating the components during the polymerization. The part used for the polymerization of D_4 contains a branch which allows reference samples to be taken. Dianionic poly(dimethylsiloxane) was prepared in part 1 of the apparatus from 27.4 g (92.6 mmol) D_4, 8.8 cm^3 (110 mmol) THF and 14.4 mmol dm^{-3} sodium naphthalene employing the above described procedure. After reactants were introduced the reactor was sealed off the vacuum line at point 8. The other side was then again attached to the vacuum line and dicationic pTHF was prepared. The operations were coordinated in such a way that the optimum conversion of both poly(dimethylsiloxane) and pTHF was achieved at the moment of combination though the polymerization times differed greatly (D_4 500 h, THF 50 h).

The solution of silenium dication was added by a syringe into the part used for THF polymerization[3], the solvent removed and THF added by distillation (25.7 g, 357 mmol) and the whole apparatus sealed off the vacuum line. The polymerization of THF proceeded at 263.1 K.

When the desired conversion was achieved a part of the solution from vessel 1 was transferred into part 2 to be used as a reference and part 2 was sealed off from part 1 at point 8a. The concentrations were adjusted to equalize the amount of remaining macroanions with that of the macrocations from the THF.

The polymerization of reference sample was then halted (by diluting with excess of methanol) and both macroionic components allowed to mix at 263.1 K by breaking the break-seal. A considerable viscosity increase was observed immediately upon mixing of both polymers; after several hours there was an observable viscosity decrease. The product was isolated 24 h after the combination by precipitating in MeOH, repeated washing with MeOH and drying to constant weight.

Molecular weight determination. Molecular weights of components and copolymers were determined osmometrically, viscometrically and/or by g.p.c. G.p.c. analyses were carried out at room temperature using a Waters

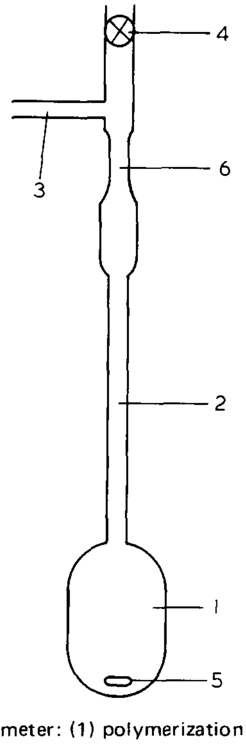

Figure 2 Dilatometer: (1) polymerization bulb; (2) precise capillary internal diameter 3 mm; (3) attachment to the line; (4) two-way stopcock; (5) stirrer; (6) seal off point

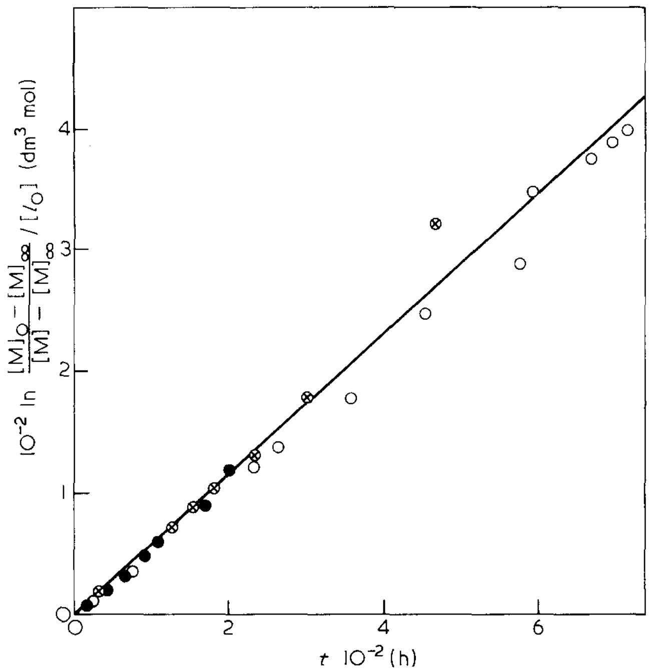

Figure 3 Dependence between variables of integrated form of equation (1): T = 263.1 K; silenium initiator concentration (mmol dm^{-3}): (●) 8.83; (⊗) 2.23; (○) 0.44

Associates instrument, the columns being packed with Styragel 10^3 nm and 10^5 nm. THF was used as the eluent at a flow-rate of 1 cm^3/min. The concentration of samples was about 0.4% w/w, the r.i. detector setting being 16 × and 8 × respectively. The calibration was made using the $\bar{M}_n$ standards of Waters Associates ranging from 1900 to 2 700 000.

A Knauer membrane osmometer was employed for the osmometric measurements, toluene at 318.1 K being the solvent.

The molecular weight of poly(dimethylsiloxane) was determined by viscometry and calculated from Mark–Houwink equation and constants derived by Barry[9].

Extraction of combination product. A powdered sample (0.5 g) was mixed with 20 cm^3 of solvent consisting of isopropanol and water (70/30 v/v). The mixture was heated on a water bath at 333.1 K while stirring occasionally. After 6 h the liquid phase was separated by decantation, the solvent evaporated at room temperature and the solid residue was weighed and analysed. During the evaporation of solvent a vessel was covered by a piece of filter paper to protect the products from dust. The evaporation was complete when a constant weight was achieved.

This procedure was repeated three times with the fraction which was insoluble in the isopropanol–water mixture. Including the insoluble fraction from the last extraction a total of four fractions was obtained*. The separation is not quantitative since the isopropanol–water system at a given concentration is capable of dissolving polytetrahydrofuran whose $\bar{M}_n$ is 15 000 (333.1 K). The interfacially active block copolymer influences the solubility of all polymer components in the system. 'Emulsions' are formed which cannot be separated without severe disturbance of the equilibrium. The fractions thus obtained can therefore be used only for a qualitative estimation of composition of combination products.

The above described procedure of drying samples to constant weight at ambient temperature and pressure is equivalent to drying *in vacuo* at 10^{-3} Pa. There are no other advantages but the procedure was adopted for its convenience.

N.m.r. spectra. N.m.r. spectra were taken on a Tesla BS 487A spectrometer. The samples were analysed at room temperature in CDCl$_3$ solutions (*ca* 10% w/v) which contained 2% additions of chloroform as the internal standard.

RESULTS AND DISCUSSION

Polymerization of THF

Our experimental arrangement allows us to take a reference sample prior to combination. The data concerning the second component are obtained indirectly from the time of polymerization and conversion. If the time dependence of THF polymerization is sufficiently well known and if this process is reproducible then a polymer possessing the desired properties can be obtained with reasonable certainty. As pTHF is a typical representative of a cationic polymer, we measured the basic kinetic data concerning its polymerization.

The rate of THF consumption obeys equation (1)[10]:

$$-\frac{d[M]}{dt}=k_p[I]_0[[M]-[M]_\infty] \qquad (1)$$

where symbols have their usual meanings. *Figure 3* compares experimental points with the integrated form of this equation. Each point was obtained in a separate experiment so that the reproducibility can also be seen. *Figure 4* shows the conversion dependence of pTHF molecular weight. Both figures indicate that the THF

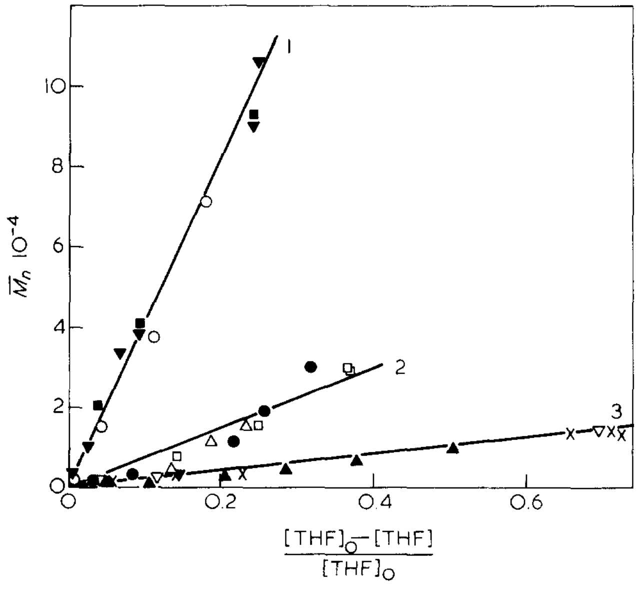

Figure 4 Dependence of molecular weight on conversion. Concentration of silenium dication in mmol dm^{-3}: (1) 0.44; (2) 2.23; (3) 8.89; polymerization temperature in K: 263.1 (▼, △, ▲); 273.1 (○, ●, X); 298.1 (■, □, ▽)

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* The immiscibility of poly(dimethylsiloxane) with other polymers was employed to separate it from other reaction components: A toluene solution of combination products (*ca.* 5%) separates to two layers during 24 h. The lower layer contains almost pure poly(dimethylsiloxane).

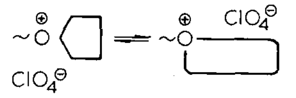
polymerization catalysed by the silenium initiator possesses the following features:

(i) fast initiation;
(ii) no termination is important in the polymerizing system;
(iii) the number of macromolecules is 5–6 times higher than the number of initiator molecules;
(iv) the value of apparent energy of activation is 40.6 kJ mol^{-1}; molecular weight of the product at a given concentration and conversion does not depend on temperature (within the temperature interval of our experiments);
(v) the polydispersity coefficient increases with temperature and polymerization time assuming value from 1.3 at 263.1 K and low conversions to 4.5 at 298.1 K and prolonged polymerization time.

The linear increase of molecular weight with conversion and the absence of termination are indicative of the living mechanism, while the formation of several macromolecules from a single dication is not.

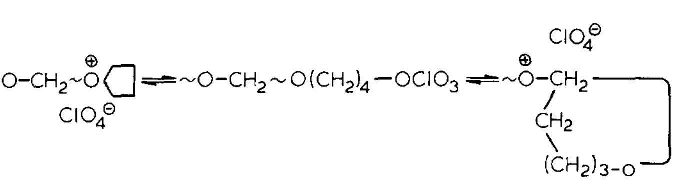
The polymerization of THF initiated by acids possessing stable counterions of type PF_6^-, SbF_6^- leads to the formation of monodisperse living polymers[11]. Unfortunately, the authors have not compared the experimental values of molecular weights with theoretical values calculated for living systems. It has been proven that cyclic products are formed during the THF polymerization[12] and that there exists an equilibrium ion (ion pair) $\rightleftarrows$ ester[13]. As reported by Plesch and Westermann[14] dioxolan, when polymerized in the presence of $HClO_4$, gives exclusively cyclic products while the use of other initiators produces more common linear macromecules under otherwise very similar conditions[15,16].

According to the rule of microscopic reversibility the size of the oxonium ring at the end of growing macromolecule will probably not be governed by a direct equilibrium



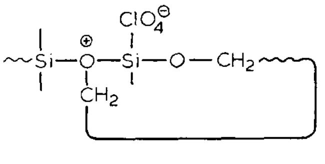
(2)

but rather by a system of equilibria, the ester or ion pair being an intermediate:



(3)

The concentration of ester may play quite an exceptional role in a big loop formation. Another reason for stimulation of the large loop formation in the polytetrahydrofuran chains may consist in their siloxane centrum with more polar –Si–O– bonds (in comparison with –C–O– bonds):



(4)

Oxonium loops are formed *via* back biting reaction (or perhaps by an analogy of end-biting reaction (4)); macrocycles may be formed by splitting-off. A concentration of macromocycles, greatly exceeding the value determined by thermodynamic factors (given by Jacobson and Stockmayer[17]) can appear in certain stages of polymerization, considering the above possibilities.

We believe that the polymerization of THF initiated by the silenium initiator is an extreme case in which the product is in form of macrocycles and dications. It is, in fact, a special example of a living polymerization where termination and transfer are absent but macrocycles are formed. Thus the concentration of macromolecules is increased and the theoretical degree of polymerization is lowered.

Direct proof of this hypothesis is not possible since difficulties arise when statistical coils formed from cyclic and linear macromolecules are to be distinguished. There is, however, strong indirect evidence. Apart from reasons mentioned[12–16] (fast initiation, no termination) the most convincing factor is seen in the high efficiency of the combination reaction of the pTHF dication with both low-molecular and polymeric dianions[18]. The efficiency of this reaction is about 95%, the multiblock copolymers being formed. These copolymers could not be formed if termination or transfer proceeded during the THF polymerization. In the former case the disappearance of cations would lead to an excess of anions during combination. These would be attached to polymer ends so that the number of blocks in the resulting polymer would be lower. If transfer processes were operative then monocations would have to be formed from dications. The monocations decrease the number of coupled blocks also.

Therefore, the higher polydispersity coefficient observed in the case of ClO_4^- catalyst may not be due to the instability of the perchlorate ion but may be attributable to the ability of this ion to create conditions favouring the formation of macrocycles.

Combination of anionic poly(dimethylsiloxane) with silenium initiator

Sodium naphthalene, when mixed with octamethylcyclotetrasiloxane, is known to produce a centre[19] growing from both ends. 'Living' anionic poly(dimethylsiloxane) prepared by means of sodium naphthalene, will grow by an order of magnitude after interaction with silenium dicationic initiator (from molecular weight 47800 to 484000). This is demonstrated in *Figure 5*, lines 1 and 3. Ionic ends of both types of chains combine and longer macromolecules of poly(dimethylsiloxane) are formed. If both anionic and cationic components are considered as 'monomer' then from the number of 'monomers' in the chain it is possible to derive the effective functionality f_E. The comparison of f_E with the theoretical functionality ($=2$) gives information about the efficiency of combination reaction (for a more detailed derivation making use of the polycondensation theory see ref 18). The above discussed combination proceeds with 95.0% efficiency.

Combination of dianionic poly(dimethylsiloxane) with dicationic pTHF

Poly(dimethylsiloxane) is absolutely immiscible with pTHF. Both homopolymers rapidly and quantitatively separate from the mixture of these polymers. The mixing of solutions of macroions gives a homogeneous mass which may be precipitated by the addition of excess methanol. Molecular weights of components and combination products are shown in *Table 1*. The determination of $[\eta]$ in the case of a reference silicon homopolymer and copolymer is represented by curves 2 and 4 in *Figure 5*. The constants for calculation of number and weight average molecular weights of copolymer by means of $[\eta]$ and g.p.c. are not known. The osmometric measurements give the value of $\bar{M}_n$ which is 5.5 times higher than the sum of both components.

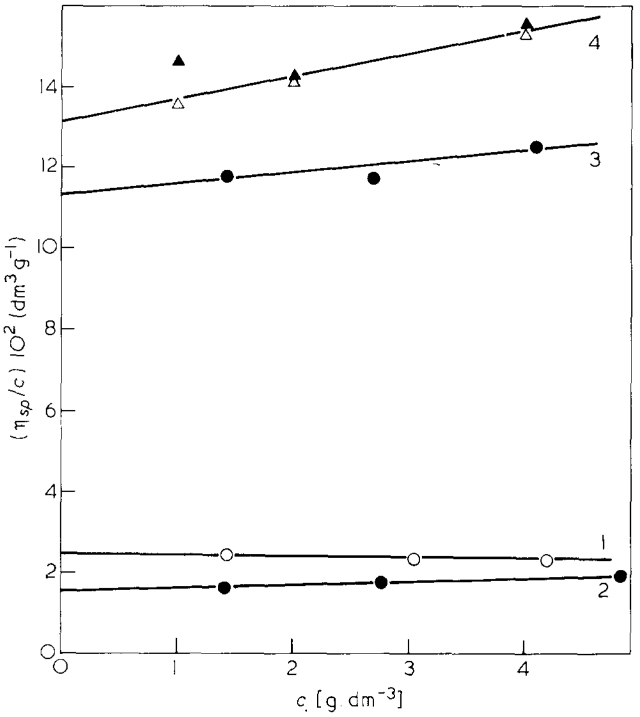


Figure 5 Dependence of η_{sp}/c vs. c for initial components and product of combination. Line 1, reference poly(dimethylsiloxane) used for the combination with silenium dication; (2) reference poly(dimethylsiloxane) for the combination with dicationic THF oligomer; (3) poly(dimethylsiloxane) formed through the combination of siloxanes (sample as in 1 + dication of $\bar{M}_n$ 500); (4) copolymer (sample as in 2 + dicationic pTHF of molecular weight 3700)

Table 1 Molecular weights of components and copolymer

Method	Molecular weight		
	pTHF	pD	Copolymer
Viscosimetry[a]	0.35	0.15	1.31
G.p.c.	3700		27700[b]
Osmometry	3600	4100	42600

[a] Values $[\eta]$ (100 cm^3/g)

[b] Calculated as pTHF

This high value was measured for the raw product which contained low molecular homopolymers. Thus the molecular weight of the pure copolymer must be much higher.

An attempt was made to employ extraction in order to obtain, at least, qualitative information about the combination product composition. The results are given in *Table 2*. The following assumptions have been made:

(i) The isopropanol/water system is capable of extracting pTHF and low molecular copolymer while polysiloxane remains in the solid state.

(ii) Since both components possess approximately the same molecular weight, both $\text{–}(\mathrm{CH_2})_4\mathrm{O}\text{–}$ and $\text{–}\mathrm{Si(CH_2)_2O}\text{–}$ are expected to be present in the copolymer in equal numbers.

(iii) No pTHF homopolymer remained in the residue after three extractions.

According to these results only 25% w/w of copolymer are present in the product of combination. Only 18.7% of overall pTHF is present in copolymer. Out of 5.4 molecules of pTHF only one molecule is dicationic. This value is in a good agreement with experimental values of molecular weight of pTHF (see the paragraph on THF polymerization). The molecular weights of individual fractions have not been measured because of difficulties with the separation of homopolymers from the copolymer.

The combination product is a white, flaky, stable material. Not even the slightest tendency of component separation was noted after a year's standing. The copolymer therefore enhances the compatibility of otherwise incompatible components.

The arrangement of $\sim\overset{|}{\mathrm{Si}}\text{–O–}\underset{|}{\mathrm{C}}$ atoms connecting siloxane and tetrahydrofuran blocks is relatively stable against hydrolysis. No hydrolysis occurs after 1 h heating in water at 333.1 K or 30 min in 0.1 N HCl at 333.1 K. Only after one hour at 363.1 K in 2 N HCl does the value of $[\eta]$ for the copolymer decrease to that of the initial homopolymers.

Table 2 Composition of combination product

Fraction	Weight of fraction [%]	Composition of fraction[a] [molar fraction D]	Distribution of components in product [%]					
			pTHF		pD			
			homo-	co-	co-	homo-	ΣpTHF	ΣpD
1	20	0.03	18.8	0.6	0.6		19.4	0.6
2	29.6	0.04	27.2	1.2	1.2		28.4	1.2
3	19.9	0.30	7.8	6.0	6.1		13.8	6.1
4	28.2	0.84		4.6	4.7	18.9	4.6	23.6
	97.7		53.8	12.4	12.6	18.9	66.2	31.5

[a] According to n.m.r. results

ACKNOWLEDGEMENTS

The authors would like to thank Drs Navrátil and Láníková for taking the n.m.r. spectra, g.p.c. analyses and osmometric measurements of the molecular weights.

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