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Anionic polymerization and copolymerization of cyclosiloxanes initiated by trimethylsilylmethyllithium

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SUMMARY

A novel initiator, i.e. trimethylsilylmethyllithium has been successfully used for the ring opening polymerization of cyclosiloxanes, in toluene or in the bulk, in the presence of the cryptand [211] or DMSO. Suitable conditions have been found in which monomodal distributions of molecular weights are observed for homopolymers of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (V_4) as well as for copolymers of V_4 with D_3 or D_4.

INTRODUCTION

Although the anionic polymerization of cyclosiloxanes has been studied for a long time, the mechanism of the process has been clarified only recently by the use of lithium cryptates as counterions (1-5). This polymerization is complicated by the presence of intra- and intermolecular reactions of the active centers on the polymer chains which lead to redistribution processes. Moreover, the nature of the living silanolate end groups is generally not well-known and fractional kinetic orders with respect to the concentration of active centers have been observed which are due to the presence of silanolate aggregates (6-8).

The anionic polymerization of cyclosiloxanes initiated by butyllithium proceeds in two steps. Firstly the silanolate $Bu[Si(CH_3)_2O]Li$, or BuDLi, is quantitatively formed in hydrocarbon solvents (9). No polymerization occurs even with a large excess of D_3 or D_4 until a donor solvent such as THF, glymes, HMPA or DMSO is added to the system. With Li^++[211], aggregates are destroyed and only one type of active species is observed, i.e. cryptated lithium silanolate ion pairs. Thus, the kinetics of propagation as well as that of cyclic by-product formation have been studied in detail for the first time, in the case of D_3, D_4, D_6 and 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (V_4) polymerizations (1-5).

We have recently shown that trimethylsilylmethyllithium, $(CH_3)_3SiCH_2Li$, can be successfully used for the ring opening polymerization of cyclosiloxanes, in toluene or in the bulk, with the cryptand [211] or DMSO as activating agents (10). Suitable conditions have been found in which monomodal distributions of molecular weights are observed, even in the case of D_4 and V_4. In this paper, we wish to report preliminary data concerning the use of $(CH_3)_3SiCH_2Li$ as initiator for the preparation of copolymers containing dimethylsiloxy (D) and methylvinylsiloxy (V) units made by ring opening copolymerization of V_4 with D_3 or D_4. Those copolymers were chosen because of their importance in cross-linking silicone rubber (11) and as precursors for the preparation of polysiloxanes bearing functional side groups.

EXPERIMENTAL

D_3, D_4 (Rhône-Poulenc), V_4 (Petrach Systems), V_3 (Silar Laboratories) as well as trimethylsilylmethyllithium (1 $mol.l^{-1}$ solution in pentane, Aldrich) were used as received. Toluene was distilled over sodium just before use, DMSO was dried over calcium hydride for one night, and the [211] ligand (Kryptofix Merck) was distilled under high vacuum. Trimethylchlorosilane (Petrarch Systems) was dried on molecular sieves 4 Å. A commercial

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**Laboratoire de Chimie Macromoléculaire associé au CNRS, URA 24 sample of a copolymer of D_4 and V_4 (Petrarch Systems) was used as a standard for ^{29}Si NMR investigation.

Polymerizations were carried out in two steps under argon, at 25°C. Monomers were fistly allowed to react with the initiator, in toluene during 3 h, in order to form quantitatively the lithium silanolate. Then the promotor ([211] or DMSO) was added to the stirred mixture and the polymerization was stopped by adding trimethylchlorosilane. Polymers were recovered by precipitation in methanol and they were then dried under high vacuum. Their average molecular weights were measured by GPC in THF on a Waters apparatus equipped for refractive index detection using a polystyrene calibration curve. Composition of the copolymers was determined by ^1H NMR: δ ($Si\text{-}C\underline{H}=C\underline{H}_2$)=5.8-6.1 ppm and δ ($Si\text{-}C\underline{H}_3$)=0.1-0.2 ppm. ^1H, ^{13}C and ^{29}Si NMR spectra were recorded in $CDCl_3$ with a AM 200 SY Bruker apparatus.

RESULTS AND DISCUSSION

Homopolymerizations of V_4 have been performed under argon at 25°C, in toluene and in the bulk, with various amounts of activating agent. The results are shown in Table 1.

Polymers have been characterized by ^1H and ^{13}C NMR. Linear polymers with the expected structure are obtained in all cases. ^1H NMR: $Si\text{-}C\underline{H}=C\underline{H}_2$ (m) (5.7-6.1 ppm); $C\underline{H}_3\text{-}Si\text{-}C\underline{H}_3$ (s) (0.1 ppm); $C\underline{H}_3\text{-}Si\text{-}CH=CH_2$ (s) (0.2 ppm). ^{13}C NMR: $Si\text{-}\underline{C}H=CH_2$ (136.7 ppm); $Si\text{-}CH=\underline{C}H_2$ (132.9 ppm); $\underline{C}H_3\text{-}Si\text{-}\underline{C}H_3$ (s) (1.0 ppm); $\underline{C}H_3\text{-}Si\text{-}CH=CH_2$ (s) (-0.8 ppm).

Monomodal distributions of the molecular weights which are quite narrow ($\overline{M}w/\overline{M}n < 2$) are observed, as shown on the GPC diagram of the polymer sample P1 (Fig.1a). The absence of cyclic oligomers (the small cyclosiloxanes are eliminated by precipitation of the reaction mixture in methanol) indicates that the polymerizations are stopped before the redistribution reactions become predominant. Moreover there is an excellent agreement between $\overline{M}n$ values measured by GPC and by osmometry (run P2), indicating that the use of a polystyrene calibration curve is perfectly convenient for polymethylvinylsiloxanes in THF.

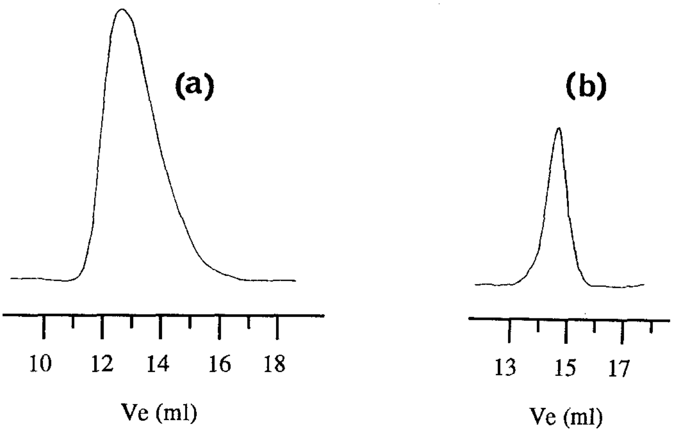


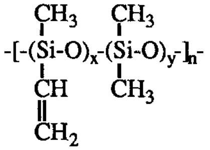
Figure 1. GPC traces of homopolymer P1 (a) and copolymer CP1 (b) in THF at 30°C.

Table 1. Homopolymerization of V_4 initiated by $(CH_3)_3SiCH_2Li$ with [211] or DMSO as activating agents, in toluene at 25°C, under argon

Run	$[M]_0$ (mol.l^{-1})	[I] (mmol.l^{-1})	Activating agent (mol.l^{-1})	t[a] (h)	Yield[b] (%)	$\overline{\mathrm{Mn}}$ [c] (GPC)	Ip
P1	1.0	12	[211]: 0.017	0.5	46	26000	1.7
P2	1.0	18	[211]: 0.026	0.5	35	19000[d]	1.9
P3	2.7[e]	12	DMSO: 0.68	17	78	65000	2.0
P4	2.6[e]	42	DMSO: 1.10	20	62	23000	1.7
P5	1.2	76	DMSO: 0.50	20	57	16000	1.7
P6[f]	2.8	189	DMSO: 0.94	1.3	73	4800	1.3

[a] Propagation time; initiation time: 3 h in all cases; [b] in polymer recovered by precipitation in MeOH; [c] in THF by using a polystyrene calibration curve; [d] $\overline{M}$ n=19000 measured by osmometry in toluene at 37°C; [e] in bulk; [f] V_3.

Table 2. Copolymerization of V_4 (M_1) with D_3 (M_2) initiated by $(CH_3)_3SiCH_2Li$ with DMSO as activating agent, in toluene at 25°C, under argon



$-[-(\overset{CH_3}{\underset{\underset{CH_2}{\|}}{\underset{CH}{|}}}{\overset{|}{Si}}-O)_x-(\overset{CH_3}{\underset{CH_3}{Si}}-O)_y-]_n-$

Run	$[M_1]_0$ (mol.l^{-1})	$[M_2]_0$ (mol.l^{-1})	X[a]	[I] (mmol.l^{-1})	[DMSO] (mol.l^{-1})	t[b] (h)	Yield[c] (%)	x[d]	$\overline{M}$ n [e] (GPC)
CP1	0.5	0.5	0.57	12.0	THF: 4.80	48	33	0.26	11000
CP2	0.7	0.7	0.57	8.7	3.60	0.5	34	0.26	10000
CP3	1.2	1.2	0.57	7.3	0.86	0.5	50	0.26	22000[f]
CP4	0.8	1.6	0.40	3.3	0.23	0.5	40	0.11	32000
CP4'	0.8	1.7	0.39	0.8_5	0.06	17	57	0.19	49000
CP5	0.6	1.8	0.31	2.0	0.16	1.0	55	0.10	38000
CP6	0.8	(D_4)2.4	0.25	1.6	0.11	44	16	0.77	62000
CP7	0.4_5	0.6	0.50	152	0.81	1.7	49	0.45	5500

[a] Molar fraction of methylvinylsiloxy units in monomers; [b] propagation time; initiation time: 3 h in all cases except for run CP7: 2h; [c] in polymer recovered by precipitation in MeOH; [d] molar fraction of methylvinylsiloxy units in copolymer determined by ^{1}H NMR; [e] in THF by using a polystyrene calibration curve; [f] $\overline{M}$ n=20000 measured by osmometry in toluene at 37°C.

The results of Table 1 show that DMSO is a less efficient activating agent than the [211] cryptand, as expected. However this much less expensive additive is able to promote the polymerization of V_4, in toluene as well as in the bulk (runs P3, P4), leading to polymers of various molecular weights, after several hours at 25°C. The rate of polymerization of the cyclic trisiloxane V_3 (run P6) is higher than that of V_4 due to ring strain effect as expected. Moreover, the molecular weight distribution is very narrow in this case: $\overline{M}w/\overline{M}n = 1.3$.

Copolymerizations of V_4 with D_3 initiated by $(CH_3)_3SiCH_2Li$ have been performed with DMSO as the activating agent, in toluene at 25°C, under argon. The results are shown in Table 2. THF is less efficient as a promoter than DMSO (runs CP1 and CP2), as expected. As in the case of homopolymerization of V_4, monomodal distributions of molecular weights which are quite narrow are observed, as shown on the GPC diagram of the copolymer sample CP1 (Fig. 1b). Again the absence of cyclic oligomers which is confirmed by ^{29}Si NMR indicates that the reaction times are short enough to prevent redistribution reactions. The agreement between $\overline{M}n$ values measured by GPC and by osmometry (run CP3) is excellent. This shows that a polystyrene calibration used for the GPC measurements in THF is convenient for these copolymers.

The molar fraction (x) of methylvinylsiloxy units (V) in each copolymer has been determined by ^{1}H NMR (Table 2). In all copolymers prepared from V_4 and D_3 (CP1 to CP5 and CP7), x is lower than the molar fraction (X) of methylvinylsiloxy units introduced in the copolymerization reaction medium. This is in agreement with the fact that the reactivity of D_3 is higher than that of V_4 (4, 12). Conversely, in the copolymer prepared from V_4 and D_4 (CP6) x is much larger than X, which is also in agreement with the relative reactivities of V_4 and D_4.

It seemed interesting to investigate the sequence distribution of repeat units in these copolymers, the properties of which strongly depend upon their microstructure. Thus the overall ^{29}Si NMR spectrum as well as enlarged regions in the spectrum of copolymer CP4 have been analyzed (Fig. 2) according to the work of Ziemelis and Saam (13) and compared to the corresponding regions in the ^{29}Si NMR spectrum of a commercial copolymer containing dimethylsiloxy (D) and vinylmethylsiloxy (V) units (PVDS) (Fig. 3). The overall spectra of the two copolymers (Fig 2a and 3a) already show significant differences in their microstructure. Indeed several peaks occurring between -18 and -19 ppm in the spectrum of the commercial sample (Fig. 3b) reveal the presence of cyclic tetramers whereas no signal appears in this region in the spectrum of CP4 showing the absence of these cyclic compounds. Assignments of the peaks in the enlarged regions corresponding to different cyclics and different comonomer sequences have been made according to ref.13.

The main difference in the microstructure of the two copolymers clearly appears from the comparison of the -34 to -36 ppm enlarged regions. Only two peaks corresponding to VV$\underline{V}$DV and VD$\underline{V}$DV sequences appear in the spectrum of the commercial sample (Fig. 3c) whereas the CP4 sample exhibits an extra peak below -35 ppm with a relatively large intensity, corresponding to VV$\underline{V}$VV sequences i.e. microblocks of vinyl units (Fig. 2b). On the other hand, the comparison of the -21 to -22 ppm regions in the spectra of the two samples shows that the relative intensity of the peak corresponding to DD$\underline{D}$DD sequences is much higher in the CP4 sample than in the commercial copolymer (Fig. 2c and Fig. 3d).

Thus the microstructure of the commercial copolymer is much closer to a statistical distribution of D and V units than the microstructure of the CP4 sample which contains a fair amount of "microblock" units.

The conclusion which can be drawn from the comparison of the ^{29}Si NMR spectra of the two copolymers is that in our experiments the reaction was stopped when the polymerization was still under kinetic control, whereas the commercial sample which contains cyclics and more scrambled units was obtained under thermodynamic control, i.e. close to equilibrium where redistribution reactions had already taken place.

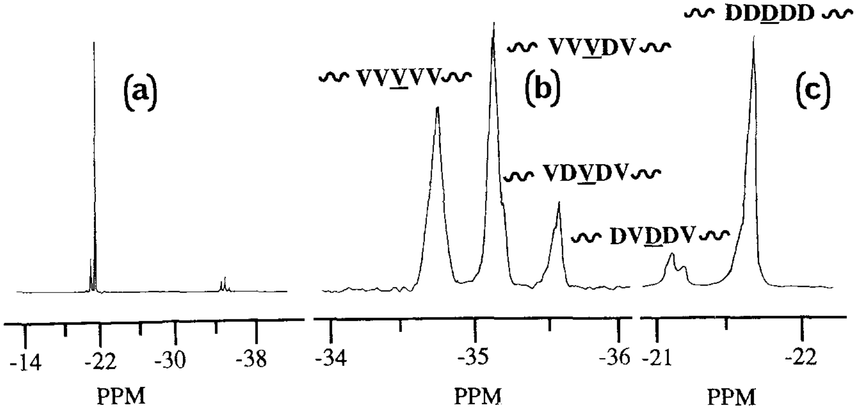


Figure 2. 39.6 MHz ^{29}Si NMR spectrum of CP4 in CDCl$_3$ at 25°C. Overall spectrum (a); enlargement of the -35 ppm region (b) and enlargement of the -21 ppm region (c) with peak assignments according to ref. 13.

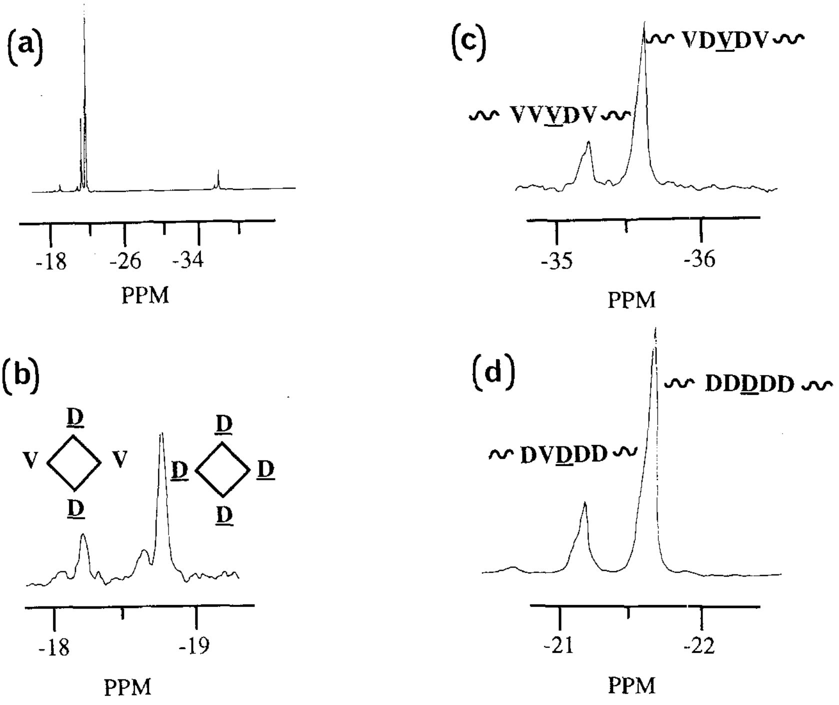


Figure 3. 39.6 MHz ^{29}Si NMR spectrum of commercial copolymer (PVDS) in CDCl$_3$ at 25°C. Overall spectrum (a); enlargement of the -18 ppm region (b); enlargement of the -35 ppm region (c) and enlargement of the -21 ppm region (d) with peak assignments according to ref. 13.

CONCLUSION

A novel initiator, i.e. trimethylsilylmethyllithium has been found to be very efficient for the ring opening of cyclosiloxanes such as D_3, D_4, V_3 and V_4, in toluene or in the bulk. Initiation proceeds rapidly at room temperature without side reactions and propagation occurs only on adding a donor agent such as the [211] cryptand or DMSO to the medium. Moreover, it is possible to find conditions in which the intramolecular redistribution reactions are not very important, thus leading to monomodal distributions of molecular weights of polymers with an index of polydispersity lower than 2. Copolymers containing various amounts of methylvinylsiloxy units can be easily prepared by copolymerization of V_4 with D_3 or D_4. The presence of "microblock" structures has been identified by ^{29}Si NMR.

Further work on the applications of trimethylsilylmethyllithium and similar compounds as initiators in the field of anionic polymerization is in progress.

ACKNOWLEDGMENT

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