Organometallic Chemistry

Metallation of poly(1-trimethylsilyl-1-prop-1-yne) and poly(vinyltrimethylsilane) with superbases

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The pathway and degree of metallation of polymers were studied depending on the the conditions (temperature, concentration, nature, and component ratio) of metallation of poly(1-trimethylsilylprop-1-yne) (PTMSP) and poly(vinyltrimethylsilane) (PVTMS) by superbases, *viz.*, Bu^nLi and Bu^sLi, in combination with potassium *tert*-pentyl oxide (Pe^tOK). For the $Bu^nLi—Pe^tOK$ system (1 : 3), the yield of modified PTMSP reached 90%. In the case of PTMSP, only the Me groups at the double bonds and at the Si atoms undergo metallation, whereas only the Me groups at the Si atoms are metallated in PVTMS. The kinetics of metallation with the $Bu^nLi—Pe^tOK$ system was studied.

Key words: metallation, polysilicon hydrocarbons, organolithium compounds, superbases, chemical modification, functionalization, poly(1-trimethylsilylprop-1-yne), poly(vinyltrimethylsilane).

Polymers containing functional groups find use as materials for semiconductor devices, optical fibers, optical discs, photomaterials, biologically active compounds, catalysts, chromatographic media, antioxidants, *etc.*[1] Functional derivatives containing the acidic —COOH or —SO_3H groups are of particular interest. These compounds can be used for the preparation of proton-conducting membranes for fuel cell systems. Poly(1-trimethylsilylprop-1-yne) (PTMSP) exhibits the record vapor and gas permeability of all the known polymers. Hence, one would expect that the introduction of functional groups into this polymer will essentially improve its separating characteristics without substantial loss of permeability, which is of importance for the membrane vapor and gas separation systems.[2,3] The preparation of derivatives of poly(vinyltrimethylsilane) (PVTMS), which also belongs to highly permeable glassy polymers,[4] is of considerable interest.

However, because of low reactivities of PTMSP and PVTMS, direct (one-step) chemical modifications of these polymers proceed in low yields and are accompanied by substantial polymer degradation.[5,6] The two-step chemical modification consisting in the metallation of the polymer followed by the replacement of the metal atom with

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the functional group could give better results due to the presence of rather acidic hydrogen atoms in these polymers.[7—9]

In the two-step modification of PTMSP with the use of Bu^nLi as the metallating agent in a polar medium or in a hydrocarbon medium in the presence of electron donors,[10—14] the degree of substitution (α) in PTMSP for the trialkylsilyl groups was at most 0.15—0.20 (mole of the functional groups per mole of the repeating unit of PTMSP) even if the metallating agent was taken in a 2—3-fold excess. The degree of substitution achieved in the modification of PVTMS[7] with the use of Bu^sLi was at most 0.12—0.15 as well.

In the present study, we used highly reactive metallating agents, *viz.*, superbases, which are also efficiently used for polymer modifications[15—19] and in organic synthesis.[20—33] Superbases[16—19] are complexes of organolithium compounds with alkoxides (Na, K, Rb, Cs), which metallate *in situ* a substrate to form a complex of the metallated substrate. Superbases for these purposes possess high reactivities (comparable with reactivities of organometallic compounds (Na, K, Rb, Cs)) and exhibit high stability comparable with that of organolithium compounds.[21]

In the present study, we examined metallation of PTMSP and PVTMS with the aim of searching for the optimum conditions of the process, revealing the direction of metallation, and controlling the reaction pathway.

Results and Discussion

Metallation of PTMSP was carried out with the use of the Bu^sLi or Bu^nLi complexes with potassium *tert*-pentyl oxide (Pe^tOK) taken in a ratio of 1 : 1 or 1 : 3. We chose alkoxide Pe^tOK as the second component because both the superbases and metallated substrates are well soluble in hydrocarbon media. For comparison, PTMSP was metallated with Bu^sLi and Bu^nLi in polar (THF) and hydrocarbon media (cyclohexane, in the case of the complex with TMEDA). The efficiency of metallation was estimated from the change in the weight after the reactions of the metallated polymer with electrophiles. The direction of metallation was determined by ^1H and ^2H NMR spectroscopy.

Quantification of the metallation process. The results of quantification of the metallation process of PTMSP (after the introduction of the Me_3Si and Me_3SiCH_2 groups) for different systems are given in Table 1. The data presented in Table 1 are averaged over several experiments, each experiment being repeated at least two times (deviations from the average values are ≤5%). We used Me_3SiCH_2Cl for the quantification of the metallation process because Me_3SiCl does not react with PTMSP metallated under the action of Bu^sLi-based systems in a hydrocarbon medium. The reaction mixtures with systems based on Bu^sLi (involved in either a superbase or a complex with TMEDA), unlike those with Bu^nLi-based systems, remained colored for more than one-and-a-half month after the addition of Me_3SiCl. In this case, products of the reaction of the metallated polymer with Me_3SiCl were not generated at all. However, metallation of PTMSP with the above-mentioned systems occurred, as evidenced by the development of the color of the reaction mixture and by the reactions of the polymer, which was metallated with these metallating agents, with CO_2 and D_2O (confirmed by IR and ^2H NMR spectroscopy).

Table 1. Degree of PTMSP metallation[a] after the insertion of the Me_3Si (I) and Me_3SiCH_2 (II) groups

Metallating agent (MA)	Medium	T/°C	PTMSP : MA	α		Y^b (%)	
				I	II	I	II
Bu^nLi	THF	0	1 : 1	0.01	—[c]	1.0	—[c]
			1 : 2	0.02	—[c]	1.0	—[c]
Bu^nLi—TMEDA (1 : 1)	Cyclohexane	65	1 : 1	0.02	—[c]	2.0	—[c]
			1 : 2	0.03	—[c]	1.5	—[c]
Bu^nLi—Pe^tOK (1 : 1)	Cyclohexane	65	1 : 1	0.83	0.73	83.0	73
			1 : 2	1.56	1.23	78.0	61
Bu^sLi	THF	0	1 : 1	0.08	—[c]	8.0	—[c]
			1 : 2	0.13	—[c]	6.5	—[c]
Bu^sLi—TMEDA (1 : 1)	Cyclohexane	65	1 : 1	—[d]	—[c]	—[d]	—[c]
			1 : 2	—[d]	—[c]	—[d]	—[c]
Bu^sLi—Pe^tOK (1 : 1)	Cyclohexane	25	1 : 1	—[d]	0.58	—[d]	58
			1 : 2	—[d]	1.08	—[d]	54

[a] Time of metallation was 2 h.

[b] Yield of the modified polymer.

[c] The value was not determined.

[d] No gain in weight was found.

Apparently, this behavior is attributed to the fact that polymer complexes metallated with the above-mentioned metallating systems did not react with rather bulky trimethylchlorosilane due to steric hindrances. Because of this, the efficiency of these systems was estimated based on the reaction of metallated PTMSP with Me_3SiCH_2Cl, which appeared to be less sterically hindered. Initially, it was found that in the case of PTMSP metallated with the $Bu^nLi—Pe^tOK$ system, the reactivity of Me_3SiCH_2Cl was close to that of Me_3SiCl (see Table 1). Upon metallation with the PTMSP—$Bu^sLi—Pe^tOK$ system (1 : 2 : 2), the degree of substitution was 1.08 and the yield was 54%. For PTMSP—$Bu^nLi—Pe^tOK$ (1 : 2 : 2), the corresponding values were 1.23 and 61%, respectively.

Hence, the metallating $Bu^sLi—Pe^tOK$ system also possesses rather high reactivity, although attempts to introduce bulky groups with the use of this system failed. It should be noted that metallation at lower temperatures proceeded more successfully than those with the use of the $Bu^nLi—Pe^tOK$ superbase resulting in a decrease in the degree of degradation of the polymer upon its modification.

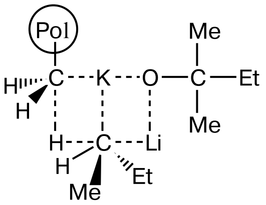
The best results were obtained with the use of the $Bu^nLi—Pe^tOK$ system (see Table 1). Metallation with this superbase (PTMSP, Bu^nLi, and Pe^tOK were taken in a ratio of 1 : 1 : 1) afforded the modified polymer in 83% yield and the degree of substitution was 0.83 (one mole of the functional groups per mole of the repeating unit of PTMSP).

The reactions with the use of organolithium compounds as such (in the absence of Pe^tOK) gave the products in very low yields (which were somewhat higher for Bu^sLi). Both in polar media and in the complex with TMEDA, the degrees of substitution were at most 0.13—0.15 even when an excess of the metallating agent was used.

It was assumed[15,27] that metallation with superbases proceeds with the formation of a complicated complex of a metallated substrate. This complex contains both bonds, *viz.*, lithium alkoxide and organometallic, *i.e.*, the reactions afford a multicenter complex of the metallated substrate:

$$R—H + Pe^tOK + R'Li \longrightarrow (R—K)(Pe^tOLi)(R'H). \quad (1)$$

The structure of this complex remains unknown. It may be considered as established that R′H is not formed upon metallation of PTMSP with the $Bu^sLi—Pe^tOK$ superbase; otherwise, there would be no difference between the action of this superbase and the $Bu^nLi—Pe^tOK$ system. Apparently, the same is true for the reaction with the use of the Bu^sLi—TMEDA complex. Below is given the assumed structure (**A**). In the case of metallation of PTMSP, this structure is produced as the final organometallic complex compound rather than as the proposed[33] transition state of the metallation process.



A

Pol is a polymer.

Effects of the temperature and polymer concentration. In the case of the $Bu^sLi—Pe^tOK$ system, metallation (which can be judged from the development of the color of the reaction mixture) proceeded successfully at room temperature. By contrast, metallation with the $Bu^nLi—Pe^tOK$ supebase at room temperature proceeded slowly to give the modified polymer in low yield (≤45—55% even after 3—4 h). The rise of the temperature to the boiling point of the reaction mixture *in vacuo* made it possible to increase the yield to 83—85%. An increase in the intensity of heating led to a decrease in the yield to ~35%, which is attributable to either decomposition of the complex of the metallated polymer or high degradation of the polymer chain under these conditions.

The polymer concentration is another factor, which is necessary to control. The concentration was chosen in such a way as to prevent an increase in the viscosity of the reaction mixture in the course of the reaction, because even a slight increase in the viscosity led to a decrease in the yield to 65—75%.

Influence of the component ratio of the $Bu^nLi—Pe^tOK$ system. We searched for the optimum conditions for the most efficient metallating $Bu^nLi—Pe^tOK$ system. Two kinetic curves were obtained for the metallation of PTMSP with the PTMSP—$Bu^nLi—Pe^tOK$ system using the components ratios of 1 : 1 : 1 and 1 : 1 : 3. As can be seen from Table 2 and Fig. 1, the degree of substitution was over 2.68

Table 2. Dependence of the degree of substitution (α) and the yield of the modified polymer PTMSP (Y)* on the reaction time for the superbases with the $Bu^nLi—Pe^tOK$ component ratios of 1 : 1 (I) and 1 : 3 (II)

Time /min	α		Y (%)	
	I	II	I	II
2	0.22	1.75	22	58
8	0.33	1.72	33	57
15	0.57	1.81	57	60
40	0.73	1.76	73	59
90	0.82	1.95	82	65
130	0.76	2.24	76	74
180	0.85	2.38	85	79
300	0.83	2.69	83	89

* Yields were determined from the gain in weight after the reaction of metallated PTMSP with Me_3SiCl.

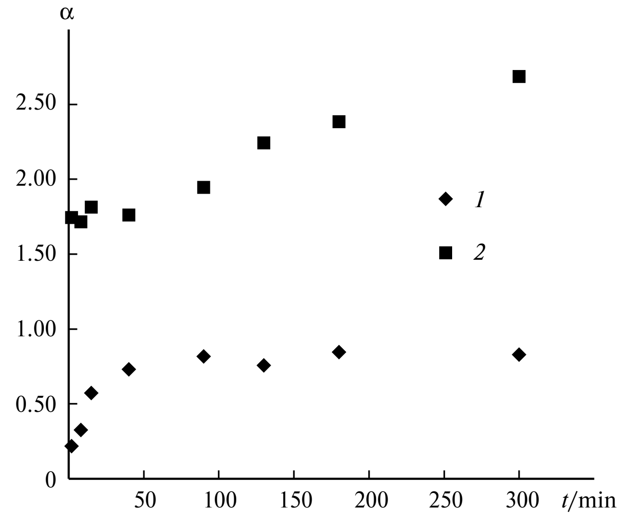


Fig. 1. Dependence of the degree of substitution (α) on the reaction time for the systems with the PTMSP—Bu^nLi—Pe^tOK component ratios of 1 : 1 : 1 (*1*) and 1 : 1 : 3 (*2*).

(one mole of the functional groups per mole of the repeating unit of PTMSP) when the components were taken in a ratio of 1 : 1 : 3 (the reaction time was 5 h). This result, which was repeatedly reproduced (see Table 2), can be explained assuming that one molecule of the organolithium compound forms a complex with three molecules of potassium alkoxide. Hence, it can be proposed that the first step of the reaction with the Bu^nLi—Pe^tOK superbase using the component ratio of 1 : 3 gives rise to a complex of the superbase with the substrate[22,29] in which Pe^tOK is involved in the metallation reaction in a stoichiometric ratio.[33]

Apparently, this process involves not only reaction (1) but also reactions (2) or (3):

$$3\ \mathrm{R{-}H} + (\mathrm{Pe^tOK})_3(\mathrm{R'Li}) \longrightarrow (\mathrm{R{-}K})_3(\mathrm{Pe^tOH})_3(\mathrm{R'Li}), \quad (2)$$

$$3\ \mathrm{R{-}H} + (\mathrm{Pe^tOK})_2(\mathrm{Pe^tOLi})(\mathrm{R'K}) \longrightarrow$$
$$\longrightarrow (\mathrm{R{-}K})_3(\mathrm{Pe^tOH})_2(\mathrm{Pe^tOLi})(\mathrm{R'H}), \quad (3)$$

because reaction (1) alone could not provide such a high yield of the modified polymer (see Table 2).

Apparently, reaction (2) can be arbitrarily considered as the reaction of potassium alkoxide with the substrate in the presence of an organolithium compound.

The plot of the degree of substitution *vs.* the time of metallation with the Bu^nLi—Pe^tOK superbase (1 : 3) has two regions, *viz.*, a "rapid" region where the degree of substitution reaches 1.80—1.90 during 15—20 min and a "slow" region where the degree of substitution approaches 2.70 in a period of a few hours. Hence, the maximum yield of the modified polymer (~89%) was achieved after 3.5—5 h. However, the polymer underwent substantial degradation in this period of time. Therefore, it can be assumed that the optimum time of modification of PTMSP with the Bu^nLi—Pe^tOK superbase is 1—1.5 h during which the yield reaches 74—76%.

It was of interest to reveal the maximum possible degree of substitution in PTMSP. Considering the two most probable directions of metallation of PTMSP, *viz.*, at one of the H atoms of three Me groups at the Si atom and at one of the H atoms of one Me group at the double bond (addition at the double bonds was considered as highly improbable), it was expected that the maximum degree of substitution in PTMSP would be at most 4.0. However, metallation with a sixfold excess of the superbase (PTMSP—Bu^nLi—Pe^tOK = 1 : 2 : 6) led to the degree of substitution of 4.70. It appeared that the replacement of the second H atom in the Me group rather than the addition at the double bond occurred under drastic conditions.

Metallation of PVTMS. We did not search for the optimum conditions for metallation of PVTMS. However, metallation of PVTMS under the conditions, which were optimum for PTMSP, also gave good results (Table 3). Metallation of PVTMS with the Bu^nLi—Pe^tOK system proceeded more slowly. Thus, a deep color of the reaction mixture involving PTMSP was developed during 2—3 min, whereas a deep color of the mixture in the reaction with PVTMS was developed during 7—10 min. Nevertheless, the degree of substitution for the Me_3Si groups achieved for PVTMS was 4.25 (4.70 for PTMSP). On the whole, the yields for PVTMS were lower than those for PTMSP at the same polymer : metallating agent ratios.

In the case of the Bu^sLi—Pe^tOK superbase, the color of the reaction mixtures containing PTMSP as well as of those with PVTMS was developed during 1—2 min. However, unlike PTMSP, PVTMS metallated with this superbase reacted with Me_3SiCl. In this case, the degree of substitution for the PVTMS—Bu^sLi—Pe^tOK system (1 : 1 : 1) was 0.43 and the yield of the modified polymer was 43%.

The reactions of various electrophiles (Me_3SiCl, CO_2, or D_2O) with metallated PVTMS proceeded more rapidly than those with PTMSP metallated under the same conditions, which is indicative of the higher reactivity of metallated PVTMS.

Table 3. Degree of PVTMS metallation[a] after the insertion of the Me_3Si groups (in cyclohexane)

Metallating agent (MA)	T/°C	PTMSP : MA	α	Y^b (%)
Bu^nLi—Pe^tOK	65	1 : 1	0.79	79
(1 : 1)		1 : 2	1.55	77
Bu^sLi—Pe^tOK	25	1 : 1	0.43	43
(1 : 1)		1 : 2	0.82	41

[a] Time of metallation was 2 h.
[b] Yield of the modified polymer.

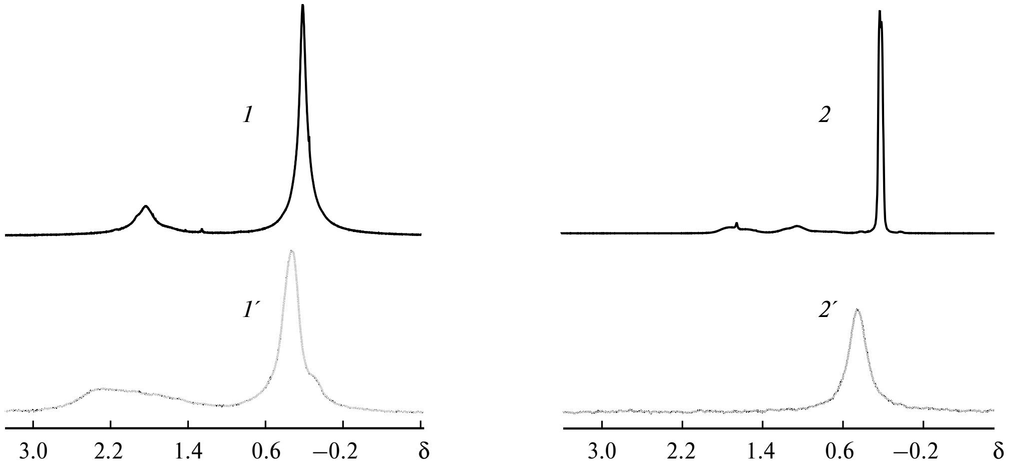


Fig. 2. ^{1}H NMR spectra of the starting polymers PTMSP (*1*) and PVTMS (*2*) and the ^{2}H NMR spectra of the deuterated polymers PTMSP (*1′*) and PVTMS (*2′*) after metallation with the Bu^{n}Li—Pe^{t}OK system (2 : 6).

Study of the direction of metallation by ^{1}H and ^{2}H NMR spectroscopy. The ^{1}H NMR spectrum of PTMSP and the ^{2}H NMR spectrum of deuterated PTMSP are shown in Fig. 2. The ^{1}H NMR spectrum of PTMSP has signals at δ 1.8 and 0.19 belonging to the hydrogen atoms of the Me group at the double bond and hydrogen atoms of the Me groups at the Si atom, respectively. The ^{2}H NMR spectra measured after metallation under drastic conditions (PTMSP : Bu^{n}Li : Pe^{t}OK = 1 : 2 : 6) also have two signals. This indicates that the substitution occurred only at two positions in the PTMSP molecule. The above-mentioned signals were assigned to the deuterium atoms of the Me group at the double bond and the deuterium atoms of the Me groups at the Si atom (signals at δ 2.2 and 0.4, respectively). In the ^{1}H NMR spectra of PTMSP, the ratio of the integral intensities of the signals of the Me—Si and Me—C=C groups is ~3 : 1, which corresponds to the ratio of the signals of nine H atoms of the Me groups at the Si atom to the signals of three H atoms of the Me group at the double bond. The direction of metallation was judged from the integral intensity ratios in the ^{2}H NMR spectra (Table 4).

The ^{2}H NMR spectra allowed us to estimate only the relative amount of deuterium in particular positions. It was impossible to determine the absolute values (by the combined processing of the ^{1}H and ^{2}H NMR spectra), because the $CH_2\underline{D}Si/CH_2\underline{D}C{=}C$ ratio was often close to the $C\underline{H}_3Si/C\underline{H}_3C{=}C$ ratio (3 : 1) and, as a consequence, the error of the determination was ±45% even if the experimental error was 5%. Hence, the degree of metallation was estimated from the results of the reactions of the metallated substrates with Me_3SiCl and Me_3CH_2Cl (from the change in the weight of the polymer) rather than from NMR spectroscopy.

It can be seen from Table 4 that for the metallating agent : PTMSP ratio varying from 1 : 1 to 3 : 1, the metallation of all systems proceeded at two positions. When the Bu^{n}Li-based systems were used, the

Table 4. Estimation of the direction of PTMSP metallation from the ^{2}H NMR spectra[a]

Metallating agent (MA)	Medium	T/°C	PTMSP : MA	$I(\underline{D}CH_2Si)/I(\underline{D}CH_2C{=}C)$[b]
Bu^{n}Li	THF	0	1 : 7	—[c]
Bu^{n}Li—TMEDA (1 : 1)	Cyclohexane	65	1 : 7	2.63
Bu^{n}Li—Pe^{t}OK (1 : 1)	Cyclohexane	65	1 : 1	2.22
		65	1 : 3	2.05
		65	1 : 6	1.57
Bu^{s}Li	THF	0	1 : 7	0.45
Bu^{s}Li—TMEDA (1 : 1)	Cyclohexane	65	1 : 1	1.51
		65	1 : 3	1.38
Bu^{s}Li—Pe^{t}OK (1 : 1)	Cyclohexane	25	1 : 1	0.64
		25	1 : 3	1.98

[a] Time of metallation was 2 h.

[b] *I* is the integral intensity of the signal.

[c] Attempts to record the spectra failed.

$CH_2\underline{D}Si/CH_2\underline{D}C{=}C$ ratio ranged from 2.05 (metallation with Bu^nLi—Pe^tOK) to 2.63 (metallation with Bu^nLi—TMEDA) for the metallating agent : PTMSP ratios varying from 1 : 1 to 3 : 1. Hence, the direction of metallation depends only slightly on the reaction conditions, the Me groups at the Si atoms being predominantly metallated. However, taking into account that the number of the Me groups at the Si atom is three times as large as the number of the Me groups at the double bond, the Me groups at the double bond are, apparently, somewhat more reactive because the ratio of the structures obtained under all conditions (in the presence of an excess or a deficiency of the metallating agent) was lower than 3.0. Moreover, an increase in the excess of the metallating agent (PTMSP : Bu^nLi : Pe^tOK = 1 : 2 : 6) led to a decrease in this ratio to 1.57. The use of the estimated degree of substitution determined for the reactions of PTMSP, which was metallated under the same conditions, with Me_3SiCl (4.75) made it possible to evaluate the degree of substitution at both positions of metallation of PTMSP. This estimate demonstrates that the degree of substitution of the Me groups at the Si atom is 2.9 for three Me groups per repeating unit, *i.e.*, the degree of substitution of one Me group is 0.97. At the same time, $\alpha = 1.85$ for the Me groups at the double bond (one Me group per repeating unit), *i.e.*, the degree of substitution is higher than unity with respect to one Me group.

In the reactions with the Bu^sLi-based systems, the direction of metallation depended much more substantially on the conditions of metallation. Thus, $\alpha = 0.45$ (predominant metallation of the Me groups at the double bond) with the use of the Bu^sLi—THF system, whereas $\alpha = 1.98$ (predominant metallation of the Me groups at the Si atom) with the use of the Bu^sLi—Pe^tOK system.

Previously,[14] it has been found that only the Me groups at the Si atom underwent metallation in the reactions of PVTMS with the Bu^sLi—TMEDA. The same result was obtained in the present study for metallation with superbases. A comparison of the ^1H NMR spectrum of the starting polymer PVTMS and the ^2H NMR spectrum of deuterated PVTMS (see Fig. 2) measured after metallation in the PVTMS—Bu^nLi—Pe^tOK system (1 : 2 : 6) showed that metallation also proceeded at one position. The degree of substitution of one Me group (taking into account that the degree of substitution is 4.25) obtained in the reaction of PVTMS, which was metallated under the same conditions, with Me_3SiCl was higher than unity (1.42).

Polymer degradation. To employ the two-step chemical modification in practice, it is important that polymers be subjected to degradation to the least extent in the course of modification. The degree of degradation can be judged from the change in the intrinsic viscosity [η]. The viscosities [η] of PVTMS and PTMSP before metallation and after the reaction of the metal-containing polymer with D_2O are given in Table 5. It can be seen that PVTMS appeared to be chemically more stable. This polymer was subjected to a lesser degradation than PTMSP. For the latter polymer, the decrease in the viscosity upon metallation with the superbases is comparable with the decrease in the viscosity observed in the reactions with the use of organolithium compounds in polar media and this value is lower than that observed upon metallation with organolithium compounds involved in the complexes with TMEDA.

Table 5. Effect of metallation on the viscosity [η] of polysilicon hydrocarbons*

Polymer—metallating agent	T/°C	$[\eta]/\text{dL g}^{-1}$
Unmodified PTMSP	—	0.53
PTMSP—Bu^nLi (1 : 1)	0	0.41
PTMSP—Bu^sLi (1 : 1)	0	0.35
PTMSP—Bu^nLi—TMEDA (1 : 1 : 1)	65	0.23
PTMSP—Bu^sLi—TMEDA (1 : 1 : 1)	65	0.25
PTMSP—Bu^nLi—Pe^tOK (1 : 1 : 1)	65	0.38
PTMSP—Bu^sLi—Pe^tOK (1 : 1 : 1)	25	0.43
PTMSP—Bu^nLi—Pe^tOK (1 : 2 : 6)	65	0.23
PTMSP—Bu^sLi—Pe^tOK (1 : 2 : 6)	25	0.31
Unmodified PVTMS	—	1.30
PVTMS—Bu^nLi—Pe^tOK (1 : 2 : 6)	65	0.87
PVTMS—Bu^sLi—Pe^tOK (1 : 2 : 6)	25	0.92

* Time of metallation was 2 h.

Experimental

The reactions were carried out *in vacuo* in all-sealed glassware vessels. The solvents and reagents were purified and then vacuum-sealed in tubes. Tetrahydrofuran was distilled first over alkali and then several times over sodium and stored over the Na/α-methylstyrene complex. Hexane and cyclohexane were distilled first over sodium and then over potassium. Butyllithium (solution in hexane, 1.6 mol L^{-1}) was used without additional purification, and Bu^sLi (solution in hexane, 2.5 mol L^{-1}) was synthesized from Bu^sCl as described previously.[34] Alkoxide Pe^tOK (solution in cyclohexane, 0.2 mol L^{-1}) was prepared from *tert*-amyl alcohol (Fluka), which was purified by distillation over sodium.[24] All organometallic compounds were titrated with 0.1 M H_2SO_4 using phenolphthalein as the indicator. Trimethylchlorosilane and TMEDA (Fluka) were recondensed into sealed evacuated tubes before use. Poly(1-trimethylsilylprop-1-yne) was synthesized in toluene in the presence of $NbCl_5$ as the catalyst; M_w and M_n were 299173—258739 and 177435—158927, respectively; the viscosity $[\eta] = 0.8$—1.5 dL g^{-1}. Poly(vinyltrimethylsilane) was synthesized in cyclohexane with the Bu^nLi catalyst; the viscosity $[\eta] = 1.3$ dL g^{-1}.

The intrinsic viscosities of solutions of the polymers in toluene were determined on an Ostwald—Ubbelode viscosimeter at 25 °C.

The direction of metallation of PTMSP and PVTMS was judged from the ^1H and ^2H NMR spectra of solutions of the starting polymers in $CDCl_3$ (for ^1H NMR) and the deuterated polymers in CCl_4 (for ^2H NMR). The chemical shifts of the signals for the H and D atoms were assigned based on the signal of $CDCl_3$. The ^1H and ^2H NMR spectra were recorded on a Bruker MSh-300 instrument (75.47 MHz); the concentration of the solutions was 20 %. ^1H NMR of the starting PTMSP, δ: 0.2 (s, 9 H, $SiMe_3$); 1.8 (s, 3 H, H(3)).

^2H NMR of deuterated PTMSP, δ: 0.5 (s, 2.9 H, H($SiMe_3$)); 2.2 (br.s, 1.85 H, H(3)).

^1H NMR of the starting PVTMS, δ: 0.03 (s, 9 H, $SiMe_3$); 0.85 (br.s, 1 H, H(1)); 1.47 (br.s, 2 H, H(2)).

^2H NMR of deuterated PVTMS, δ: 0.03 (s, 4.25 H, H($SiMe_3$)).

Metallation of polymers (general procedure). A reaction vessel equipped with a magnetic stirrer, an appendix with a ground stopper, and tubes with breakable membranes containing trimethylchlorosilane and solutions of Bu^nLi and Pe^tOK was evacuated for 3—4 h and heated several times with a gas burner. Then the apparatus was filled with dry argon and disconnected from the vacuum apparatus. Poly(1-trimethylsilylprop-1-yne) (0.542 g, 4.83 mmol) was placed in the reactor. The reactor was again evacuated, heated several times with a gas burner, and sealed off from the vacuum line. A solution of Pe^tOK in cyclohexane (25.0 mL, 0.2 mol L^{-1}) was introduced into the reactor through a glass membrane. The concentration of the solution was chosen in such a way that no additional amount of the solvent was required for dissolution of the polymer. Poly(1-trimethylsilylprop-1-yne) was dissolved with vigorous stirring and heating for ~20 min, after which Bu^nLi or Bu^sLi (3.0 mL, solution in hexane, 1.61 mol L^{-1}) was placed in the reactor. Hence, the final component ratio for the PTMSP—Bu^nLi—Pe^tOK system was 1 : 1 : 1. After 1—2 min, the reaction mixture turned dark and opaque, and the dark color became deeper during the next 20—30 min. After metallation for 2 h, a threefold excess of trimethylchlorosilane with the respect to the total amount of lithium- and potassium-containing compounds was added. After several hours, MeOH was added to the reaction mixture. The yield was 83%. The degree of substitution was 0.83.

References

1. A. Akelah and A. Moet, *Functionalized Polymers and Their Applications*, Chapman and Hall, London, 1990.
2. N. A. Platé, A. K. Bokarev, N. E. Kaliuzhnyi, E. G. Litvinova, V. S. Khotimskii, V. V. Volkov, and Yu. P. Yampol´skii, *J. Membr. Sci.*, 1991, **60**, 13.
3. N. A. Plate, E. M. Antipov, V. V. Teplyakov, V. S. Khotimskii, and Yu. P. Yampol´skii, *Vysokomol. Soedin., Ser. A*, 1990, **32**, 1123 [*Polym. Sci. USSR*, *Ser. A*, 1990, **32**, 1053 (Engl. Transl.)].
4. N. A. Platé, S. G. Durgarjan, V. S. Khotimskii, V. V. Teplyakov, and Yu. P. Yampol´skii, *J. Membr. Sci.*, 1990, **52**, 289.
5. K. Nagai, A. Higuchi, and T. Nakagawa, *J. Appl. Polym. Sci.*, 1994, **54**, 1207.
6. K. Nagai, A. Higuchi, and T. Nakagawa, *J. Appl. Polym. Sci.*, 1994, **54**, 1353.
7. V. M. Vorontsov, V. S. Khotimskii, S. G. Durgar´yan, and A. M. Krapivin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1147 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1980, **29** (Engl. Transl.)].
8. USSR Inventor's Certificate No. 1133851, *Byul. Izobr.*, 1992, 41 (in Russian).
9. P. V. Pivovarov, E. V. Vorontsov, and V. S. Khotimskii, *Tez. dokl. Vseros. konf. "Kremniiorganicheskie soedineniya: sintez, svoistva, primenenie"* [*Abstrs. of Papers, All-Russian Conf. "Organosilicon Compounds: Synthesis, Properties, Application"*], Moscow, 2000, L52 (in Russian).
10. Y. Nagase, K. Sugimoto, Y. Takamura, and K. Matsui, *J. Appl. Polym. Sci.*, 1991, **43**, 1227.
11. Y. Nagase, S. Mori, and K. Matsui, *J. Polym. Sci.*, *Part A: Polym. Chem.*, 1988, **26**, 3131.
12. Y. Nagase, K. Ishihara, and K. Matsui, *J. Polym. Sci.*, *Part B: Polym. Phys.*, 1990, **28**, 377.
13. Y. Nagase, T. Ueda, K. Matsui, and M. Uchikura, *J. Polym. Sci.*, *Part B: Polym. Phys.*, 1991, **29**, 171.
14. Y. Nagase, S. Mori, and K. Matsui, *J. Appl. Polym. Sci.*, 1989, **37**, 1259.
15. J. H. G. Steinke, S. A. Haque, and J. M. J. Fréchet, *Macromolecules*, 1996, **29**, 6081.
16. L. Lochmann and J. M. J. Fréchet, *Macromolecules*, 1996, **29**, 1767.
17. L. Lochmann, K. L. Wooley, P. T. Ivanova, and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1993, **115**, 7043.
18. L. Lochmann, J. M. J. Fréchet, K. L. Wooley, and V. Smigol, *Polym. Mater. Sci. Eng.*, 1993, **69**, 426.
19. L. Lochmann and J. M. J. Fréchet, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1993, **33**, 588.
20. L. Lochmann and J. Trekoval, *J. Organomet. Chem.*, 1987, **326**, 1.
21. L. Lochmann and J. Trekoval, *Collect. Czech. Chem. Commun.*, 1988, **53**, 76.
22. W. F. Bailey and E. R. Punzalan, *J. Am. Chem. Soc.*, 1994, **116**, 6577.
23. F. Faigl and M. Schlosser, *Tetrahedron Lett.*, 1991, **32**, 3369.
24. L. Lochmann, H. Jakubuv, and L. Brandsma, *Collect. Czech. Chem. Commun.*, 1993, **58**, 1445.
25. M. Schlosser, *Pure Appl. Chem.*, 1988, **60**, 1627.
26. M. Schlosser and S. Strunk, *Tetrahedron Lett.*, 1984, **25**, 741.
27. D. Wilhelm, T. Clark, P. v. R. Schleyer, J. L. Courtneidge, and A. G. Davies, *J. Am. Chem. Soc.*, 1984, **106**, 361.
28. R. A. Benkeser, A. E. Trevillyan, and J. Hooz, *J. Am. Chem. Soc.*, 1962, **84**, 4971.
29. R. Lehmann and M. Schlosser, *Tetrahedron Lett.*, 1984, **25**, 745.
30. L. Lochmann and J. Petranek, *Tetrahedron Lett.*, 1991, **32**, 1483.
31. W. Bauer, B. Brix, C. Schade, and P. v. R. Schleyer, *J. Organomet. Chem.*, 1986, **306**, C1.
32. A. A. Arest-Yakubovich, I. V. Zolotareva, N. I. Pakuro, E. V. Kristal´nyi, and B. I. Nakhmanovich, *Vysokomol. Soedin., Ser. A*, 1996, **38**, 418 [*Russ. Polym. Sci.*, *Ser. A*, 1996, **38**, 241 (Engl. Transl.)].
33. L. Lochmann, *Eur. J. Inorg. Chem.*, 2000, 1115.
34. H. Gilman, W. Moore, and F. W. Baine, *J. Am. Chem. Soc.*, 1941, **63**, 2479.

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