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Degradative side reactions in the syntheses of exactly alternating silarylene-siloxane polymers

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Dedicated to Professor Dragutin Fleš on the occasion of his 70th birthday

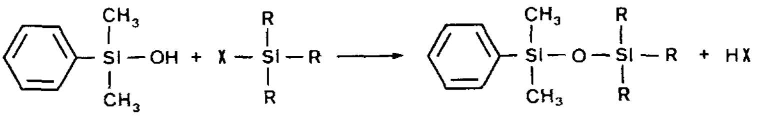
SUMMARY

Four principal synthetic methods for preparation of exactly alternating silarylene-siloxane polymers: the chlorosilane, the acetoxysilane, the aminosilane and the ureidosilane polymerization reactions, were compared under equivalent experimental conditions. As indicated earlier, polymers with considerably different molecular weights were obtained. The highest molecular weight polymer resulted from the ureidosilane reaction, while the lowest ones were obtained from the chlorosilane and the acetoxysilane routes. Because thorough precautions were taken to ensure equally favorable conditions in all preparations, these results seem to support a hypothesis that the latter two reactions are limited by the occurrence of degradative desilylation side reactions which are inherent to the nature of these polymerization systems.

INTRODUCTION

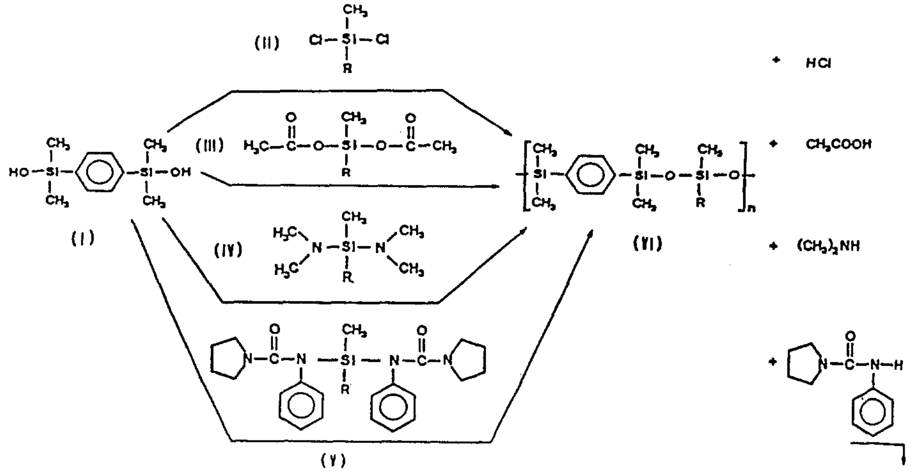
Exactly alternating silarylene-siloxane polymers (1), such as VI, can be prepared by four principal polymerization reactions, known as chlorosilane (2-3), acetoxysilane (4), aminosilane (5-6) and ureidosilane (7) synthetic routes, shown in Reaction Scheme 2.

In all these polymerizations, the basic reaction is a nucleophilic displacement at silicon in which silanol nucleophile attacks the silane to form a Si-O-Si unit, as follows:



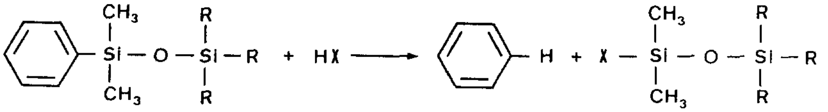
(1)

This reaction is a relatively fast process at usual polymerization temperatures (which normally range from about -20°C to about 25°C), so that all four polymerization reactions of Scheme 2 occur rapidly and provide practically quantitative yields of reaction products (normally above about 90-95%). However, it has been observed (1) that molecular weights of structurally same polymers obtained by these polymerization reactions could be greatly different with respect to the polymerization route chosen for preparation, so that various polymers prepared by different investigators had degrees of polymerization which ranged from less than 50 for the products obtained by the chlorosilane reaction to above 1 000 for the polymers prepared by the aminosilane and the ureidosilane routes (1).



Reaction Scheme 2

To explain these differences, it has been suggested (5-7) that in these polymerization systems polymer molecules may undergo degradative chain scission through side reactions with polymerization by-products, and that one such side reaction might be desilylation at the C_{Ar}-Si main chain polymer bonds, as follows:


(3)

However, it is very well known that high molecular weight polymers can be obtained by polycondensation reactions only if certain strict requirements imposed by the step growth character of these polymerization processes are precisely satisfied. These requirements include: (1) the use of highly purified monomers, solvents and atmosphere; (2) the exact adjustment of the stoichiometric ratio of concentrations of the reacting functional groups; (3) proper selection of the reaction conditions which would allow very high conversions; and, when the former are satisfied, (4) effective prevention of possible side reactions in which either: (a) reacting functional groups may irreversibly be used up so as to unbalance effective ratio of their concentrations, or (b) polymer molecules may undergo degradative chain scission resulting in the lowering of their already attained degree of polymerization. Because of this, a hypothesis that degradative side reactions may occur in the chlorosilane and the acetoxysilane polymerization systems so as to allow formation of only low molecular weight silarylene-siloxane polymers, would gain support if it could be clearly shown that the observed large differences in molecular weights of their polymer products would also appear when all four synthetic routes for preparation of these polymers are compared under equivalent experimental conditions which would satisfy all mentioned requirements of step growth polymerization reactions and favor formation of as high as possible molecular weight products. Such a comparative analysis was the subject of this work.

EXPERIMENTAL

1,4-bis(dimethylhydroxysilyl)benzene, I, was purchased from Petrarch Systems Silanes and Silicones and used in polymerization reactions without further purification.

Dimethyldichlorosilane (Aldrich) was purified by fractional distillation under nitrogen and the fraction which boiled at 70°C was used.

Dimethylamino(dimethyl)silane and bis(N,N-tetramethylene-N'-phenylureido)dimethylsilane were prepared according to the previously reported procedures (6,7).

Polymerization solvents: THF, toluene and chlorobenzene, were purified according to the previously described procedures (3,6,7).

All polymerization reactions were performed using the so-called silane deficient method (5-7). A typical procedure used was described earlier (7). Every care was taken to simulate this procedure in each polymerization reaction as close as possible. In all cases, reactions were started with 10 mmol of solid disilanol into which 50 mL of respective disilane solutions containing 9.5 mmol of the silane monomer were added during 2 hours at -20° to 0°C. After this was completed, reaction mixtures were allowed to warm up to room temperature, and portions of the silane solutions, containing 0.5 to 0.2 mol % of the stoichiometrically required amounts, were incrementally added until the highest possible molecular weight polymers were obtained. The increase in polymer molecular weight during the course of this second stage of polymerization reactions was monitored by GPC, according to the previously described method (7). All reactions were carried out until no further change in polymer molecular weight could be detected after at least three consecutive additions of 0.2 mol % portions of the silane monomer. The obtained polymer products were isolated from the reaction mixtures by precipitation and drying; reprecipitated from tetrahydrofuran and dried again. Their molecular weights were redetermined by GPC, and in all cases they agreed with those determined at the end points of polymerization reactions within about 10 %.

RESULTS AND DISCUSSION

The above described experimental procedure for polymerization reactions compared in this work, was chosen in desire to ensure that all four synthetic routes were performed under equivalently favorable conditions for preparation of as high as possible molecular weight polymers. With respect to that, the key factor was the second stage of this procedure, during which precise titrations of unreacted silanol functional groups were performed by incremental additions of well defined aliquots of the silane monomers until the end-point of each polymerization reaction was reached. This was judged by using a GPC monitoring method, which allowed to follow shifting of the growing polymer peaks towards higher molecular weights during the course of each polymerization reaction and to continue titrations until these peaks ceased to shift further when equimolarity of the reacting functional groups was reached and polymers with highest possible molecular weights were obtained. Of course, in order to ensure equivalent degrees of purity of the monomers used, the same disilanol batch was employed in all polymerization reactions, and purity of solvents and silanes was verified by GC and by ^{1}H NMR to exceed at least 99 %.

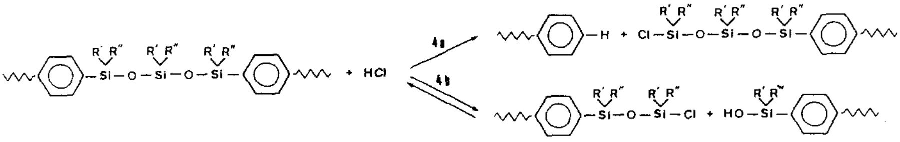
Hence, with all these precautions taken, it could be accepted that experimental requirements for preparation of high molecular weight polymers were satisfied equally well for all four polymerization systems compared, and, since it had already been shown by previous investigators (1) that high conversions were characteristic for all of them, occurrence of unfavorable side reactions would indeed seem to be the only remaining reason for differences in polymer molecular weights if these repeatedly appeared.

The results obtained are shown as degrees of polymerization in Table 1.

It can be seen from these data that the highest molecular weight polymer was obtained by the ureidosilane polymerization reaction, somewhat lower by the aminosilane reaction and considerably lower by both the chlorosilane and the acetoxysilane polymerization routes. In addition to this, it can also be seen that chlorosilane route yielded considerably higher molecular weight product when a stream of inert gas was bubbled through the polymerization reaction mixture during entire course of preparation.

Both of these observations suggest that the reasons responsible for significantly lower molecular weight polymers obtained from the chlorosilane and the acetoxysilane reactions are inherent to these polymerization systems, while either absent, or at least severely restricted in the aminosilane and the ureidosilane ones. Therefore, occurrence of degradative side reactions which would be favored in the former, but restricted in the latter systems could indeed appear quite possible cause of the observed behavior.

Two such reactions involving either polymer C_{Ar}-Si, or Si-O bonds can be envisioned, as shown in the following equation:



Of these, the siloxane cleavage reaction (4b) would not be expected to result in any substantial decrease of resulting polymer molecular weight, because both Si-OH and Si-Cl ends formed are very reactive under the conditions to which these systems are exposed, so that they should reenter into the condensation process and the most one can expect is perhaps a slight disturbance of exact alternation of

TABLE 1
Degrees of polymerization of Polymers VI, obtained by reactions of Scheme 2 *

Polym. Route	Solvent	DP_w e.p.	DP_w is.	DP_w/DP_n e.p.	DP_w/DP_n is.
chlorosilane	Tl	49	58	3.45	1.92
	THF**	91	98	3.1	1.95
acetoxysilane	Tl	57	62	2.89	1.9
aminosilane	Tl	855	912	3.12	1.95
ureidosilane	Cb	1240	1285	2.65	1.85

* Tl: toluene; Cb: chlorobenzene; e.p.: at polymerization end point; is.: isolated product.
** With stream of N_2 bubbling through the reaction mixture.

silarylene, Si-Ar-Si-O-, and siloxane, Si-O, polymer groups. This leaves desilylation reaction (4a) as the most probable reason for the observed behavior, and this can be rationalized as follows. Cleavage of the C_{Ar}-Si bond is a well known general reaction of organosilicon chemistry and it normally occurs very readily with electrophilic agents while relatively rarely with the nucleophilic ones (8,9). It is an electrophilic aromatic substitution, which is generally fast, often proceeds quantitatively, and can be utilized preparatively and even analytically. The most reactive agents in this reaction are aqueous hydrogen halides, particularly HCl, but even in non-aqueous media, such as those used in polymerization systems considered in this work, the reaction proceeds quite well. Its rate increases with concentration of HCl but it decreases for compounds which contain oxygen bound to silicon. Electron donating substituents on silicon, such as methyl groups for example, increase the sensitivity of the C_{Ar}-Si bond towards cleaving, because of more negative charge in the neighborhood of silicon in the transition state than in the initial one.

Consequently, in systems such as the chlorosilane and the acetoxysilane polymerization reactions described in this work, all conditions are clearly quite favorable for occurrence of this reaction, and it is indeed difficult to see why the polymerization by-products should not be able to attack the C_{Ar}-Si bonds either in the disilanol monomer or in the silarylene-siloxane polymer molecules as shown by Reactions 3 and 4a. In either case, non-reactive Si-C_6H_5 chain ends would be formed and condensation reactions would be prevented at these ends. Therefore, two competing reactions: (1) the polymer forming polycondensation (Reactions 2) and (2) the polymer breaking desilylation (Reaction 4a), would simultaneously take place and molecular weights of the resulting polymers would be decreased relative to what they would be if desilylation did not occur. The magnitude of this decrease would depend on the effectiveness of the polymerization by-product to attack the C_{Ar}-Si main chain polymer bonds and the higher that effectiveness the lower would be the obtained polymer molecular weight. Therefore, less reactive polymerization by-products would offer better chance for preparation of truly high molecular weight polymers.

Judging by the results described, the effectiveness of the polymerization by-products in decreasing the silarylene-siloxane polymers molecular weight can be represented by the following order:

$$HCl > CH_3COOH > R_2NH > R_2N-C(O)-N(C_6H_5)H$$

It follows from this order that HCl appears as the most reactive agent of the series in decreasing polymer molecular weight. This agrees well with its already mentioned pronounced activity in causing desilylation reactions in general. In another agreement with this, the formation of higher molecular weight polymer in the chlorosilane polymerization system through which inert gas was blown during the course of polymerization reaction, can be attributed to apparent ability of that gas to sweep out some HCl so as to reduce its concentration in the polymerization reaction mixture.

In contrast to two acids, however, weakly basic dialkylamines and particularly virtually neutral phenylureas clearly appear less reactive in decreasing polymer molecular weight, and because of that, for preparation of silarylene-siloxane polymers in general, including exactly alternating members of this family in particular, the chlorosilane and the acetoxysilane routes should be avoided and the ureidosilane route should be chosen whenever truly high molecular weight polymers are desired.

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