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Functionalization of Living Polymers via Ethoxysilane Based Compounds: Synthesis and Interaction with Silica Particles

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Summary: To optimize the reaction of ω-carbanionic styrene or butadiene/styrene polymers with ethoxysilane based compounds, the influence of several experimental parameters on the orientation of the functionalization reaction and its yield was examined. The resulting end-functionalized polymers were systematically investigated by SEC, ^{1}H NMR and elementary analysis. The orientation of the reaction was found to be directly depending on the chemical nature of the chain end and / or on the type of additive (ethers, LiCl). Best results were obtained with tetraethoxysilane, provided the functionalization is conducted around 5°C, and the active chain end of isoprenyl type. These reactions were extended to bifunctional polymers, the reaction product of butyllithium with m-diisopropenylbenzene being used as an initiator. The efficiency of this initiator for the synthesis of well-defined bifunctionalized polydienes almost quantitatively fitted with three alkoxy functions at both chain ends was demonstrated. Some preliminary results on the mechanical properties of mixtures of functionalized polymers with silica were mentioned.

Keywords: anionic polymerization; bifunctional initiator; ethoxysilanes; functionalization; rubber

Introduction

The improvement of performance of tires has been a continuous challenge in the last hundred years. In such materials, three components play an important role: The styrene-butadiene rubber polymer (SBR) eventually functionalized, the presence of polymers exhibiting other topologies such as star-shaped structures and the filling agent. In carbon black based materials, extensively used as filling agent until recently, crosslinking is achieved upon formation of sulphide bridges and the chains strongly interact with carbon black. The

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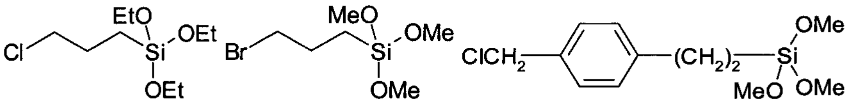
replacement of carbon black in rubbers by silica-based compounds has been shown to still improve their properties. One limitation of the system is due to the fact, that in rubbers charged with silica, phase separation may occur due to the non-compatibility between the rubber (SBR chains) and the polar groups of the silica surface. The heterogeneous dispersion of silica may also contribute to phase separation. To overcome these difficulties several solutions were introduced with more or less success: Use of selected silica compounds who do not aggregate, silica based polysulphide crosslinking agents linking the rubber matrix to silica and /or anionically synthesized SBRs[1-4]. The use of SBRs prepared by anionic polymerization and quantitatively fitted at one or better at the two chain ends with polar groups may represent an interesting alternative[5,6]. The polar group should interact with the surface of the silica particles and, therefore, limit the mobility of the chain ends.

The major part of the present work deals with a systematic investigation of the functionalization reactions of ω-carbanionic polymers with various heterofunctional micromolecular species, such as (3-chloropropyl)triethoxysilane, in order to design polymers fitted quantitatively at one chain end with alkoxysilane functions. The extension of the reaction to bifunctional polymers will also be discussed, the prerequisite being a bifunctional initiator, efficient and stable even in the present of polar additives. Some preliminary results on the behavior of ethoxysilane functionalized SBRs mixed with silica will be mentioned.

Functionalization of monofunctional polymers with ethoxysilanes

End-alkoxylated polymers have been shown to be well adapted for the surface modification of silica particles. Contrary to end-functionalized polymers having isopropyloxydimethylsilyl end-groups[7], silyl-ether functions can be hydrolyzed also with bases, whereupon grafting on the hydroxyl functions of the silica particles can be achieved and stable covalent Si-O-Si bonds created. In addition, the presence of the polymer chain on the silica particles favors their dispersion and should prevent them from aggregation. Once crosslinked, the mobility of the polymer chain is largely restricted and improved mechanical properties of the rubbery materials are expected. As mentioned above, anionic polymerization is the method of choice to achieve these functionalization reactions. In the following, we first examined the reaction of ω-carbanionic polymers with (3-chloropropyl)triethoxysilane (1), the chlorine function of the $Cl\text{-}CH_2$- group being the deactivating site. We tested several other ethoxysilane based compounds (3-bromopropyl)trimethoxy or triethoxysilane (2), 2-(3,4-cyclohexyl)ethyltrimethoxysilane, *o*-/*p*-chlorophenyltrimethoxysilane (3), tetraethoxysilane (Figure 1). Most of these compounds exhibit moderately hydrolysable groups. Therefore, the attack of the ethoxysilane function by the living polymer during the functionalization reaction should be prevented.



(1) (2) (3)

Figure 1 . Structures of some deactivating agents

Monocarbanionic polymers : polystyrene (PS), polybutadiene (PB) and styrene/butadiene copolymers (SBR) were synthesized in hydrocarbon medium either in the presence or without ether (1,2-diethoxyethane) according to well-established procedures. We examined the influence of the following parameters who may directly affect the orientation of the functionalization reaction: Nature of the chain end (styryllithium, α-methylstyryllithium, diphenylalkyllithium, butadienyllithium, isoprenyllithium), steric hindrance, functionalization temperature, polar additives (potassium alcoholates), salts (LiCl)... The reaction has been schematically represented in Figure 2.

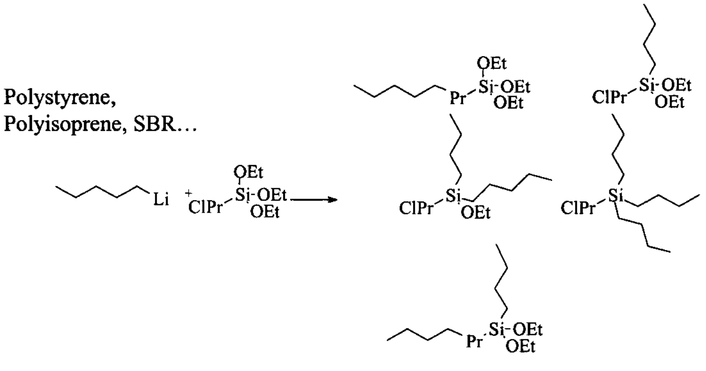
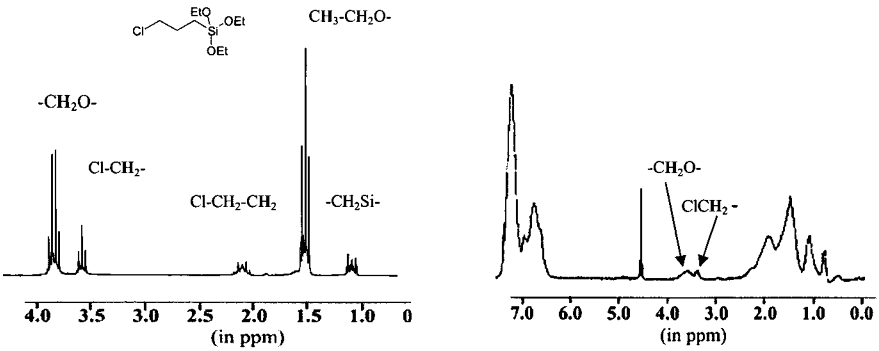


Figure 2 . Schematic representation of the deactivation reaction with component 1

Functionalization with (3-chloropropyl)triethoxysilane

We first examined the functionalization of low molar mass ω-carbanionic PSs wit (3-chloropropyl)triethoxysilane. Chemical titration and ^{1}H NMR were extensively used to achieve that aim. In addition, Size Exclusion Chromatography (SEC) characterization was performed on all the samples to determine the amount of coupling product whenever present. The following conclusions could be drawn from these experiments :

For living polystyrenes, over a temperature range from 0 to 60°C, both the chlorine function and the ethoxy group have reacted as it is revealed from ^{1}H NMR measurements (Figure 3 b). The amount of coupling product remains low provided the reaction temperature is kept below 60°C. The chain ends of the polystyrene were also modified by an intermediate addition of isoprene before coupling with (3-chloropropyl)triethoxysilane. Under these conditions even at 60°C no coupling product was detected by SEC. Therefore, no substitution of the chlorine function was noted, whatever the temperature was. This can be explained by the lower reactivity of the chain end.

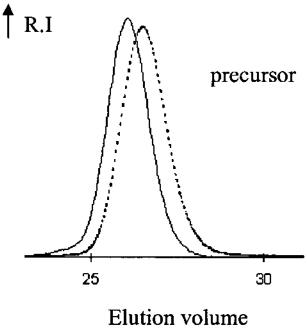


a) b)

Figure 3 . ^{1}H NMR measured in $CDCl_3$ a) : component (1), b) : PS functionalized with (1)

These preliminary results prompted us to study, among the different parameters, the influence of the nature of the chain end on the efficiency and the orientation of the coupling reaction. The polystyrene chain end was modified by an intermediate addition of 1,1-diphenylethylene (DPE) to lower its reactivity. These PSs were reacted in pure benzene with

(3-chloropropyl)triethoxysilane. In that case, quantitative reaction of the chain end with the chlorine function of the deactivating agent was noted (Figure 4 and 5). This confirms earlier results obtained by Quirk[8].



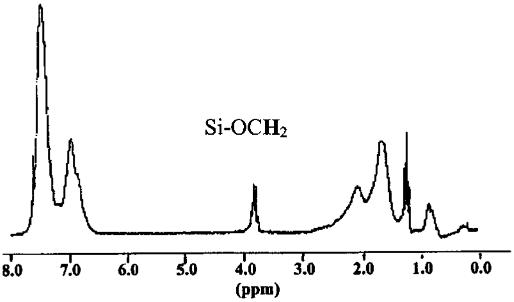


Figure 4 . SEC traces of a PS sample Figure 5 . ^{1}H NMR of the same PS (200MHz-$CDCl_3$)

To control the composition i.e. the statistical incorporation of styrene in SBR based materials and the microstructure, the reaction may be conducted in the presence of ether or of an alkali alcoholate. On another hand, the presence of that ether may enhance the reactivity of the chain end and could affect the orientation of the functionalization reactions. To verify that point, ω-carbanionic polybutadienes or polystyrenes were reacted with (3-chloropropyl)-triethoxysilane) in the presence of ether. In fact, SEC characterization confirmed the presence of high amounts of coupling products and chain-end analysis evidenced the implication of the chlorine and the ethoxy functions in the functionalization process.

Along the same line, we modified the chain ends with α-methylstyrene end groups. This compound should not polymerize at the selected reaction temperature, but its presence should enhance the reactivity of the chain end. The addition reaction was followed by UV spectroscopy. Once quantitative addition was observed, (3-chloropropyl)triethoxysilane was introduced in the reaction medium. SEC characterization confirmed the decrease of the amount of coupling product over a temperature domain from 0 to 60°C. In fact only partial substitution of the chlorine function was noted and at least one ethoxy function was involved in the process leading to a mixture of mono to tetra substituted species. The addition of ether does not improve the results: No reaction with the chlorine function was detected, quantitative substitution of one ethoxy function was noted.

The presence of LiCl has been shown to improve the polymerization of alkyl(meth)acrylates and to limit the occurrence of side reactions. Therefore, we performed a series of functionalization reactions in the presence of LiCl : The amount of coupling product could be reduced, but no reaction at all on the chlorine function was observed.

Functionalization with other triethoxysilane based compounds

We attempted also functionalization reactions with (3-bromopropyl)triethoxysilane and with 2-(3,4-epoxycyclohexyl)ethyltrimethoxylsilane. As in the case of the chloro compound, selected polymers PS, SBRs with various chain ends were synthesized and their functionalization subsequently performed. In most cases, no quantitative functionalization could be achieved. In addition the amount of coupling product was much higher.

From these studies the following conclusions could be drawn : As expected, in most cases, the chlorine and the ethoxy functions of the micromolecular compound are involved in the process. The orientation of the reaction is directly depending on the chemical nature of the chain end and on the type of additive (ethers, LiCl): For polymers fitted with styryllithium, α-methylstyryllithium or diphenylmethyllithium chain ends, in the presence of ether the chlorine function is only partially substituted, and the ethoxy group is also involved in the process. In the case of isoprenyllithium chain ends, only one ethoxy group is substituted.

Functionalization with tetraethoxysilane

In preliminary experiments, we showed that the functionalization of PBLi or SBRLi with tetraethoxysilane (TES) yielded species exhibiting three ethoxy functions at the chain end, and also high amounts of coupling product. To try to increase the content of trifunctional product, we used higher concentrations of deactivating agent, i.e. a five molar ratio with respect to the concentration of living chain ends. The reaction is schematically represented in Figure 6. Under these conditions, provided the functionalization is conducted between 0 and 10°C and the active chain end of isoprenyl type, three ethoxy functions could be quantitatively introduced at the chain end. Some characterization data are given in Table 1.

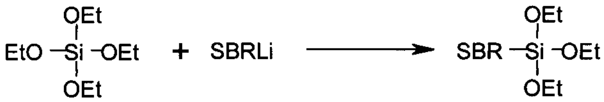


Figure 6. Schematic representation of the functionalization of SBR's with tetraethoxysilane

The reduction of the amount of coupling product with increased ratio [LE] to [TES] is confirmed unambiguously by SEC (Figure 7).

Advantage of the reaction was also taken to synthesize tetrafunctional star-shaped polymers based on TES and containing a central Si atom. It has been reported in the literature that, upon addition of living polymers to $SiCl_4$ under appropriate conditions, grafting can be realized. Strong differences in reactivity were yet observed depending upon the nature of the chain end. When PSLi is reacted with $SiCl_4$, a mixture of trifunctional (74 %) and tetrafunctional (26 %) species was detected by SEC, whatever the polarity of the solvent was. The reaction time was 48 hours in benzene at 50°C or in a mixture of benzene /THF). On the contrary when conducted in cyclohexane at 50°C and with a short polybutadiene spacer at the chain end, four arm star-shaped polymers could be obtained. We made similar observations when tetraethoxysilane was used as a coupling agent instead of $SiCl_4$ (Table 1).

Table 1 . Characterization data of SBRs functionalized with TES (5 molar excess)

Reference	SBR1	SBR1A	SBR2B	SBR3A	SBR3B
Polar Additives	Bis-Ether			Bis-Ether//Potassium Alcoholate	
[TES]/[Li]	5	-	5	-	5
$M_{n,\,th}$ ($g.mol^{-1}$)	80 000	80 000		80 000	
M_w (SEC/LS)	87 000	87 000	89 000	95 000	105 000
P (PS/RI)	1,12	1,08	1,11	1,11	1,2
Styr. Content %	15 %	9 %		9 %	
Microstructure (^1H NMR)	(1,2) : 39% (1,4) : 61%	(1,2) : 44% (1,4) :56%		(1,2) : 34% (1,4) : 66%	
Main product (SEC)	87 %	-	93 %	-	89 %
Funct. Yield	100 %	-	99 %	-	99 %

SBRA and SBRB correspond respectively to the precursor and the functionalized product

P(PS/RI) : polymolecularity based on refractive index detection (SEC)

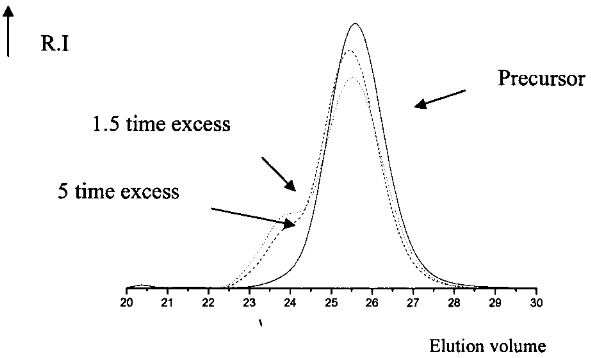


Figure 7 . SEC traces of the reaction product of a SBR chain with tetraethoxysilane

Extension to bifunctional polymers

The replacement of monofunctionalized SBRs by SBRs quantitatively functionalized at both chain ends with ethoxy groups would still improve the mechanical properties of SBR / silica materials. The prerequisite for an efficient functionalization is the existence of a bifunctional initiator allowing the controlled synthesis of the α,ω-living SBR precursors. However, until now, no bifunctional initiator, exhibiting carbon-lithium bonds and yet soluble and efficient in hydrocarbon solvents has proved really satisfactory for the synthesis in the presence of ethers of α,ω-bifunctional SBR elastomers. Many years ago, one of us[9] has used the reaction of a stoichiometric amount of *sec*-butyllithium (BuLi) to one molecule of m-diisopropenylbenzene (DIB) to produce a bifunctional initiator, which is soluble in non-polar solvents. In the absence of polar additives, this initiator has been shown to be quite efficient for the polymerization of isoprene and butadiene and the subsequent synthesis of well-defined elastomeric materials. More recently similar work was done along that line10). Provided m-DIB is reacted with BuLi at high temperature, no polymerization should occur. Therefore no oligomeric species should be formed. In the present work, the reaction of BuLi with m-DIB was studied in the presence of different types of ethers at a temperature such as to prevent DIB polymerization. The reaction is schematically represented in Figure 8.

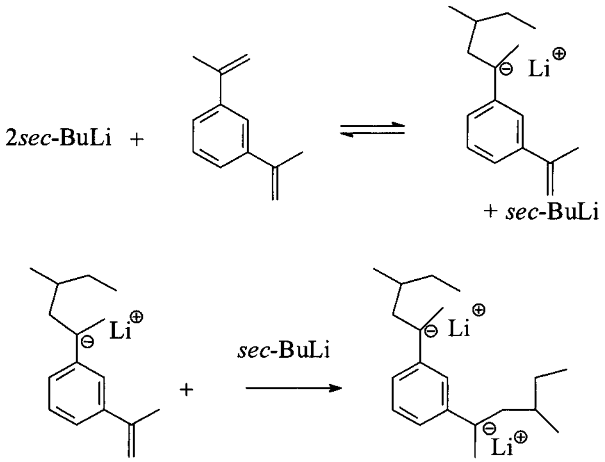


Figure 8 . Schematic representation of the reaction of m-DIB with 2 *sec*-BuLi

-We examined first the reaction in hexane (or in cyclohexane) in the presence of selected ethers (1,2-diethoxyethane ...) at 60°C. At that temperature no propagation of DIB should occur and the reaction limited to the addition of two BuLi to one DIB unit. The reaction products were examined by SEC and mass spectroscopy. The presence of the diadduct in higher quantities than under identical conditions in the absence of polar additives could be confirmed. The amount of diadduct formed was found to be directly related to the DIB concentration.

It was also of interest to investigate the kinetics of this reaction to establish whether the reactivity of the two double bonds with respect to BuLi is the same or not and, whether the bifunctional initiator once formed is stable, especially in the presence of ether. The reaction product is characterized by the presence in UV spectroscopy of a maximum of optical density around 320 nm (Figure 9). Therefore, the evolution of the optical density versus time could be followed directly and the influence of the reaction conditions on the nature of the products formed could be determined.

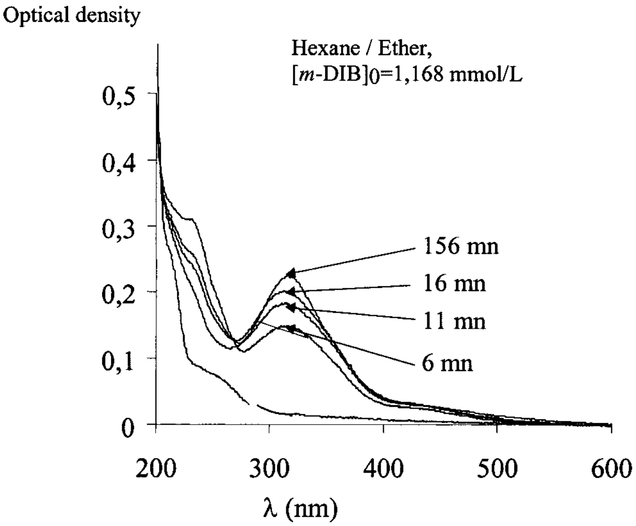


Figure 9 .Evolution of the optical density versus reaction time for the addition of *sec*-Buli onto m-DIB. (60°C, [*m*-DIB]$_0$=1,168 mmol/L)

Active site titration evidenced that the concentration of living sites is lower than the initial concentration of *sec*-BuLi. Therefore, that concentration corresponds to the concentration of diadduct determined by other methods. When the reaction is conducted at 40°C, high quantities of oligomers are formed during the first stage of the reaction as it can be seen by SEC measurements (Figure 10). After some time the amount of diadduct increases.

Selected reaction products were used for the polymerization of styrene. They were also tested for the (co-)polymerization of dienes with styrene. Conditions were identical to those employed for the polymerization of the same monomers with butyllithium. From the characterization of the resulting polymers, it can be concluded that :

- This initiator is efficient, since the polymer samples obtained exhibit narrow molar mass distributions and, in most cases, quite symmetric molar mass distributions, which indicates that the initiation process is rapid and quantitative.

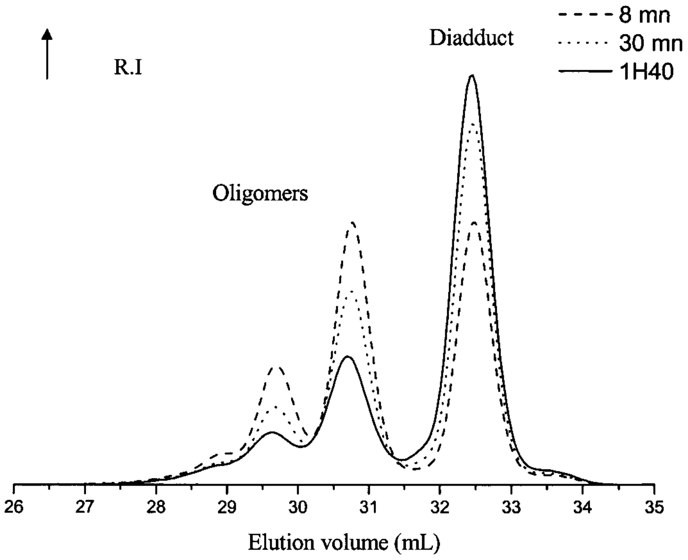


Figure 10 . SEC traces of the reaction products of 2 *sec*-BuLi /*m*-DIB at 40 °C (Hexane : 300mL ; DIB : 5,83 mmol ; sec-BuLi : 11,66 mmol ; ether: 0,58 mL)

- That initiator is bifunctional, since the molar masses calculated using the mole ratio monomer converted to initiator are close to the measured number average molar masses. Account has yet to be taken of the concentration of bifunctional initiator really present in the medium. This statement does not originate solely from comparisons between experimental and calculated molar mass.

- The "bifunctionality" of the living polymers was also verified by reacting them with a stoichiometric amount of α,α'-dibromo-*p*-xylene. The observed increase of the molar mass of the resulting chain extension product with respect to the precursor, by a factor of 10, is a strong indication in favour of the bifunctional nature of the precursor. In addition, the values of the radii of gyration are comparable to those observed for linear polymers of similar molar masses. Reaction of the living polymer with divinylbenzene resulted in network formation. Gel formation generally occurs at room temperature in less than 1 hour.

- Addition of ethylene oxide to the medium yields reversible gel formation. Once deactivation is achieved by introduction of methanol, the medium gets again soluble. The presence of the OH functions was confirmed by UV titration after modification with naphtyl-1-isocyanate. That point will be discussed in a forthcoming paper. Functionalization of these polymers with ethoxysilane-based compounds was achieved according to the strategy developed for monofunctional polymers.

Table 2 . Characteristics of functionalized polymers used in viscosimetry studies

Reference	M_n g.mol^{-1} (SEC)	M_w/M_n (SEC)	Wt.- % main product	Funct. yield	Styrene % (molar)	(1,2) % (molar)
SBR1A [a)]	1630	1.09	-	-	13	84
SBR1B [a)]	1820	1.2	82	93	13	84
SBR 2A [b)]	2350	1.09	-		11	-
SBR 2B [b)]	2500	1.11	-	100	11	-
SBR 3A [c)]	2230	1.09	-		14	83
SBR 3B [c)]	2540	1.22	78	97	14	83
SBR 4A [d)]	2250	1.15	-	-	11	-
SBR 4B [d)]	2470	1.18	90	100	11	-

a) Functionalized with component 1
b) SBR-Si-$(OEt)_2PrCl$
c) SBR-$Si(Oet)_3$
d) SBR-PI-$Si(OET)_3$

SBRA and SBRB correspond respectively to the precursor and the functionalized product

In some preliminary studies we could show that the mechanical properties of mixtures of functionalized polymers with silica are improved as compared to systems where unfunctionalized polymers were used. The characteristics of the sample are given in Table 2 and the viscosity behavior is represented in Figure 11. Further work has to be done along that line.

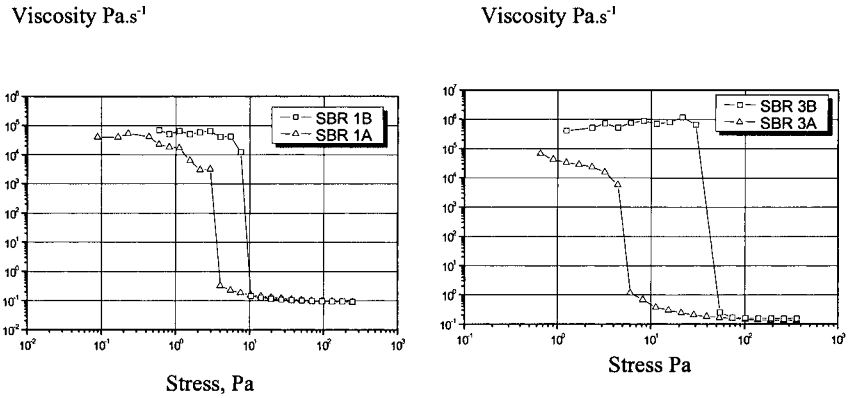


Figure 11 . Evolution of the viscosity versus stress for selected SBR samples (see Table 2)

Conclusion

In the present work, the functionalization of α- or α,ω-living polystyrenes or related polymers with ethoxysilane derivates in hydrocarbon solvents has been examined. It has been shown that the nature of the chain end and /or the presence of additives in the reaction medium directly influence the orientation of the reaction. For polymers fitted with styryllithium or α-methylstyryllithium living chain ends only partial substitution of the chlorine function has been observed, whereas with isoprenyllithium end groups, only substitution of one ethoxy group occurred. On the contrary, provided appropriate experimental conditions are used the reaction of tetraethoxysilanes with monofunctional polymers lead to quantitative substitution of one ethoxy function. Once the functionalization conditions optimized for monofunctional polymers, they have been extended to bifunctional polymers. Based on the reaction of sec-butyl lithium with m-diisopropenyl benzene an efficient bifunctional initiator stable and efficient even in the presence of ether has been obtained. These polymers, characterized by well-controlled molar and by sharp molar distributions have been functionalized almost quantitatively with ethoxy groups. Some preliminary results on the solid-state behavior of these polymers in the presence of silica have been presented. More detailed information on the last point will be given in a forthcoming paper.

Acknowledgments

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