Synthesis and characterization of polystyrenes fitted with either pendent or chain end hydroxyethyl functional groups

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Functional polystyrenes fitted with hydroxyethyl groups at chain ends or as statistically distributed pendent functions along the polymer backbone were prepared, using anionic methods. Functionalization of the polystyrene chain was achieved by metallation followed by the reaction of the metallated sites with ethylene oxide and subsequent protonation. Fractionation of the resulting polymer was required to eliminate branched species formed in a side reaction. The functionality of the polymers was accurately determined by u.v. spectrometry on the labelled samples.

(Keywords: functional polystyrene; hydroxylated polymers; labelling of hydroxyl groups; hydroxy group determination)

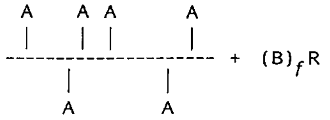
INTRODUCTION

In spite of the extensive investigations reported in the literature dealing with structure–property relationships in polymer networks and the interpretation of network behaviour with rubber elasticity theories, many questions still remain unanswered.

As well as 'statistically' crosslinked systems[1–8], 'model' networks obtained by coupling α,ω-functional precursor chains ('endlinking') with plurifunctional reagents[9–16] were used for these investigations.

Endlinking: A----------A + $(B)_fR$ with $f \geqslant 3$

Statistical:



$$\text{---}\overset{A}{|}\text{--}\overset{A}{\underset{A}{|}}\text{--}\overset{A}{|}\text{----}\underset{A}{|}\text{--}\overset{A}{|}\text{---} + (B)_fR \quad \text{with } f \geqslant 2$$

One surprising difference between statistical and endlinked networks which was observed in many instances was the difference in mechanical behaviour. In particular, ultimate properties, such as elongation at rupture, are much poorer in endlinked systems. This represents one of the drawbacks of liquid rubber materials, which are inferior compared to traditional rubbers. Several authors assigned the observed effect to the narrower distribution of elastic chain lengths[12,15,17]. The difference in behaviour could also reflect a possible difference in the network topology[18,19], which might be related to the presence of defects in the system, their nature and importance. Investigations concerning such network defects were reported quite recently in the literature.

To carry out a comparative investigation on statistical and endlinked networks, crosslinking should be performed by means of a comparable chemical reaction, so that the interchain links are of the same chemical nature. This is the case of the classical condensation reaction between an alcohol function and an isocyanate, with formation of a urethane group, the widely applied reaction to prepare polyurethanes. Thus, di- and tri-isocyanates can be used as crosslinking agents, with polystyrenes with chain end or pendent hydroxyethyl functions as precursor polymers.

In this paper the synthesis and characterization of well defined functional polystyrenes fitted with these hydroxyl groups are described.

EXPERIMENTAL

Solvents and reagents

Tetrahydrofuran (THF) was first distilled over sodium wire and then treated with sodium benzophenone. Distillation from this organometallic solution under argon atmosphere yields dry THF, which is stored under slight argon pressure.

Cyclohexane was dried over sodium wire and distilled under argon. It was then treated with sec-butyllithium in the presence of a trace of styrene. Appearance of the characteristic orange–red colour of the styryl carbanion indicates that all protonic impurities are eliminated. Dry cyclohexane, recovered from this solution by distillation, is stored under argon atmosphere.

Tetramethylethylenediamine (TMEDA) (99%, Aldrich) was distilled under argon in the presence of sec-butyllithium.

Organometallic compounds

Potassium dihydronaphthylide was used to initiate the anionic polymerization of styrene yielding α,ω-dicarbanionic species. An initiator solution in THF

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($\sim$0.5 mol l^{-1}) was prepared according to the usual procedure. The exact concentration was determined immediately before use by titration with pure acetanilide.

Sec-butyllithium was prepared in cyclohexane solution at a 0.75 mol l^{-1} concentration according to the classical method. This organometallic reagent was preferred to n-butyllithium, since in the presence of TMEDA the latter is able to cleave the polystyrene chain.

Monomers

Styrene (99%, Merck) was distilled twice over sodium wire under reduced pressure just before use and directly collected in a burette under argon.

Ethylene oxide (99.8%, Fluka) was degassed several times over sodium wire and collected directly into a Schlenk device by cold wall distillation.

Synthesis of functional polymers

Polymerizations were carried out in THF at low temperature (-70°C) under slight argon pressure, in a perfectly closed 2 l glass reactor. The polymerization device was purged before use by heating under vacuum and by vacuum–argon cycles. The solvent is introduced and some drops of the initiator solution are added until persistence of the light green colour, in order to neutralize all traces of protonic impurities. After addition of the required amount of initiator solution, the styrene is introduced dropwise. The polymerization is accompanied by a slight temperature increase. When the polymerization reaction is terminated, the temperature decreases and stabilizes again at -70°C. The 'living' carbanionic chain ends are then either deactivated by the addition of some drops of methanol or transformed by the 'endcapping' reaction. The polymers are precipitated and washed in methanol and dried at 80°C under reduced pressure.

Endcapping of polystyrenes

Endcapping of the polymer with hydroxyethyl groups is achieved after addition, at -70°C, of a large excess of ethylene oxide (four to six times the stoichiometric amount) to the vigorously stirred α,ω-dicarbanionic polystyrene solution. After 1–2 min, gel formation occurs due to the association of the alcoholate chain ends formed in the ring opening reaction. The medium is then maintained at -20°C for $\sim$12 h. At this temperature polymerization of ethylene oxide does not occur, thus only one monomeric unit is added at the polystyrene chain ends[20,21]. When the characteristic red colour of the benzylic carbanion has vanished, the addition of a small amount of methanol ($\sim$5 vol%) provokes the dissociation of the chain ends due to the transformation of potassium alcoholate into alcohol end groups and the physical gel collapses immediately. The solution is then neutralized with a few drops of hydrochloric acid, filtered and the polymer precipitated in methanol. For further purification the polymer is redissolved in THF, precipitated in methanol and dried at 50°C under reduced pressure.

Synthesis of polystyrenes fitted with pendent hydroxyethyl functions

Functionalization of polystyrene with pendent hydroxyethyl groups can be achieved according to a method described in the literature[22,23]. It proceeds in two steps. First, a polystyrene precursor is metallated by sec-butyllithium, in the presence of TMEDA[24]. Then, in a second step the metallated sites of the polymer are reacted with ethylene oxide, which yields pendent ethoxyalcoholate sites and, after protonation, hydroxyethyl groups.

The metallation reaction is carried out in the same reactor as used above for anionic synthesis, under slight argon pressure, since the same experimental conditions concerning 'protonic' impurities are required. The following example illustrates this synthesis: polystyrene (65 g), prepared by anionic polymerization, with a number average molecular weight $\bar{M}_n = 53\,000$ g mol^{-1} ($\bar{M}_w/\bar{M}_n = 1.01$) was dissolved in dry cyclohexane (1350 ml) at a temperature close to the θ-temperature (34.5°C). A few drops of styrene in the solution act as an indicator: traces of protonic impurities introduced into the medium with the polymer are neutralized by slow addition of the sec-butyllithium solution until appearance of the red colour of the benzyl carbanion, which has to persist at least for 2 h. Then a known amount of the organometallic solution is rapidly introduced, followed by the addition of the quantity of TMEDA required for the metallation reaction. A plurilithiated polymer is thus formed which precipitates partially after a few minutes. Within $\sim$3 h the metallation reaction goes to completion. Functionalization to form lithium ethanolate is then achieved by rapid addition of a large excess of ethylene oxide (three to four times the stoichiometric quantity) to the heterogeneous reaction mixture. The reaction is continued overnight. The colour of the medium fades to pale yellow, as often observed in the presence of alcoholates. The modified polymer is treated with acetic acid, after addition of THF, to ensure homogeneity. The polymer solution is washed with water to eliminate the lithium salt and the functionalized polymer recovered by precipitation in methanol. Purification requires a second precipitation and finally the polymer is dried under reduced pressure.

Treatment of the functional precursor polymers

As already pointed out, functional polymers are to be used in network synthesis based on the reaction between hydroxyethyl and isocyanate groups. This synthesis requires very dry conditions, since the isocyanate function is sensitive to moisture. To ensure efficient drying, the precursor polymers are redissolved in benzene, the water traces eliminated by azeotropic distillation and the dry polymers recovered by lyophilization.

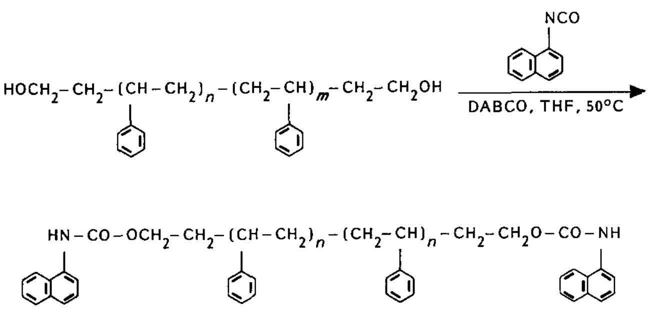
Polymer characterization

Molecular weights and molecular weight distributions were determined by size exclusion chromatography (s.e.c.), using an apparatus equipped with two microstyragel columns (pore size in the range of 50–105 Å) and with refractometric, u.v. (262 nm) and low angle laser light detection (LALLS)[25]. The light scattering device was a Chromatix CMX 100 (wavelength: 633 nm). Polystyrene standards in the molecular weight range 1900 to 3×10^6 g mol^{-1} were used for calibration. The elution solvent flow rate (THF) was 0.8 ml min^{-1} and the polymer sample injected was 0.2 ml of a 0.5–4 g l^{-1} THF solution.

Functional group analysis

The number of hydroxyethyl functions per polymer chain was determined by two methods: titration by the classical phosgenation method[26]; u.v. spectrometric determination, after labelling the hydroxy groups with a chromophore, using a Shimadzu u.v.-visible 220 Graphicord.

The second method, which was perfected in our laboratory, requires a modification of the hydroxyl groups by reacting them with 1-naphthylisocyanate, as follows:



$$HOCH_2{-}CH_2{-}(CH{-}CH_2)_n{-}(CH_2{-}CH)_m{-}CH_2{-}CH_2OH \xrightarrow[\text{DABCO, THF, 50°C}]{}$$

$$HN{-}CO{-}OCH_2{-}CH_2{-}(CH{-}CH_2)_n{-}(CH_2{-}CH)_n{-}CH_2{-}CH_2O{-}CO{-}NH$$

The chromophore is thus attached to the polymer chain by means of a urethane link.

The above method is illustrated by the following example: carefully dried α,ω-dihydroxyethyl polystyrene (1 g) and five times the stoichiometric amount of 1-naphthylisocyanate were dissolved in dry THF (3 ml) at 50°C. The catalyst used was diazobicyclooctane (DABCO). The reaction, which has to be carried out under argon to avoid any traces of moisture or oxygen, goes to completion after 4–5 h. The polymer is then precipitated and washed in methanol. However, the excess naphthyl compound is not yet completely eliminated. Therefore the polymer has to be redissolved in THF, precipitated and washed in methanol, an operation to be repeated until no more free labelling compound remains in the sample. This is the case when it is no longer detected in the precipitation solvent by u.v. spectrometry. The u.v. absorption spectrum of the labelled polystyrene presents two peaks: one, at 296 nm, corresponding to the naphthylcarbamate absorption; and the second peak, of stronger absorption at 262 nm, resulting from the more abundant phenyl groups (*Figure 1*). The quantitative analysis of the u.v. spectra requires the knowledge of the molar extinction coefficient of the chromophore group. Therefore a model molecule, 1-naphthylcarbamatephenyl ethylene ($C_{10}H_9{-}NH{-}CO_2{-}C_2H_4{-}C_6H_5$), had to be prepared. In THF solution this compound follows the Beer–Lambert law up to a concentration of 1.4×10^{-4} mol l^{-1}. Its molar extinction coefficient in THF at 296 nm is 7100 l mol^{-1} cm^{-1}.

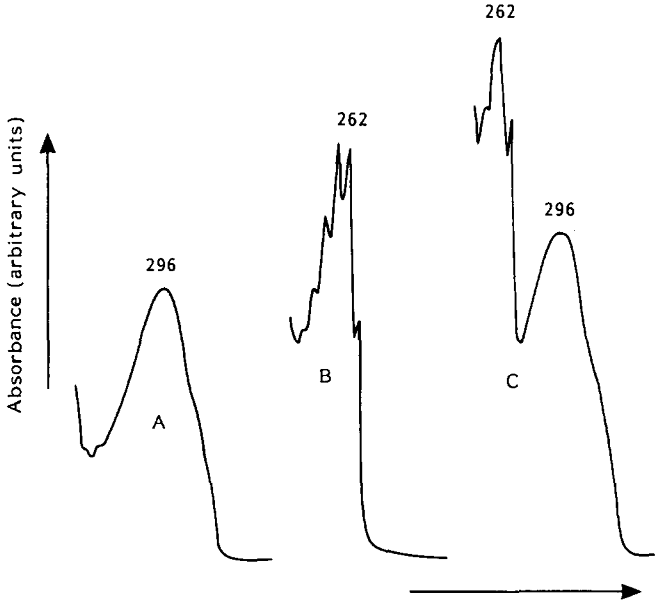


Figure 1 U.v. absorption spectra of: (A) model compound; (B) α,ω-dihydroxyethyl polystyrene; (C) functional polystyrene after labelling with naphthylisocyanate

RESULTS AND DISCUSSION

Synthesis of α,ω-dihydroxyethyl polystyrenes

A series of α,ω-difunctional polystyrenes was prepared as described above and their molecular characteristics obtained by s.e.c. The number of hydroxyethyl groups was determined by both methods, phosgenation titration and u.v. spectrometry after labelling with naphthylisocyanate. The results are shown in *Table 1*. One of our objectives was to establish, by means of these well defined samples, the most adequate method to determine the number of hydroxyl functions attached to the polymer. The results shown in *Table 1* indicate clearly that the accuracy of the determination of the percentage of hydroxyl groups in the polymer, by the classical phosgenation method, is very poor. Indeed, comparison of the number average molecular weights calculated on the basis of the data given by the hydroxyl analysis, with those obtained by s.e.c., shows rather striking discrepancies. Thus, this method is revealed to be inadequate and cannot be applied to the functional group analysis of our polymers.

On the contrary, calculation of the number of molecular weights based on the concentration of the labelled hydroxyl groups, given by spectrometric analysis, yields values which are consistent with the number average weights and the expected functionality (2) of these samples. Of course this method requires very careful elimination of the free naphthyl compound, since only traces of remaining labelling agent would lead to an overestimation of functional groups and an underestimation of the molecular weight.

The excellent agreement between the number average molecular weights determined by s.e.c. and calculated on the basis of the u.v. spectrometric values indicates also that the labelling of the hydroxyl functions by reacting them with the isocyanate compound is practically quantitative. This implies that under the experimental conditions used the contribution of possible side reactions is negligible.

Considering the above results, we decided to apply, in the following, the latter method to the characterization of the polystyrenes with pendent hydroxyethyl functions.

Synthesis of polystyrenes fitted with pendent hydroxyethyl functions

As a starting polymer polystyrene with a molecular weight $\bar{M}_n = 53\,000$ g mol^{-1} ($\bar{M}_w/\bar{M}_n = 1.01$), prepared by anionic polymerization (*Figure 2a*), was used. The functionalization was carried out according to the procedure described in the Experimental section. The

Table 1 Characteristics of α,ω-dihydroxyethyl polystyrenes

Sample	$\bar{M}_w$[a]	$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n^{u.v.}$[b]	$\bar{M}_n^{a}/\bar{M}_n^{u.v.}$	OH[c] (%)	$\bar{M}_n^{Ph}$[d]
PSH1	6100	5900	1.03				
PSH2	11 100	11 000	1.01				
PSH3	16 200	16 100	1.01				
PSOH1	5700	5500	1.04			0.795	4277
PSOH2	10 200	10 000	1.02			0.595	5714
PSOH3	15 500	15 200	1.02			0.445	7640
PSN1	6200	5900	1.05	5700	1.04		
PSN2	10 500	10 000	1.05	9600	1.04		
PSN3	15 700	15 200	1.03	15 200	1.00		

[a] Determined by s.e.c.-LALLS (g mol^{-1})
[b] Determined by u.v. spectroscopy on labelled samples
[c] Determined by phosgenation titration
[d] Calculated on the basis of the data given by the hydroxyl analysis (phosgenation titration)

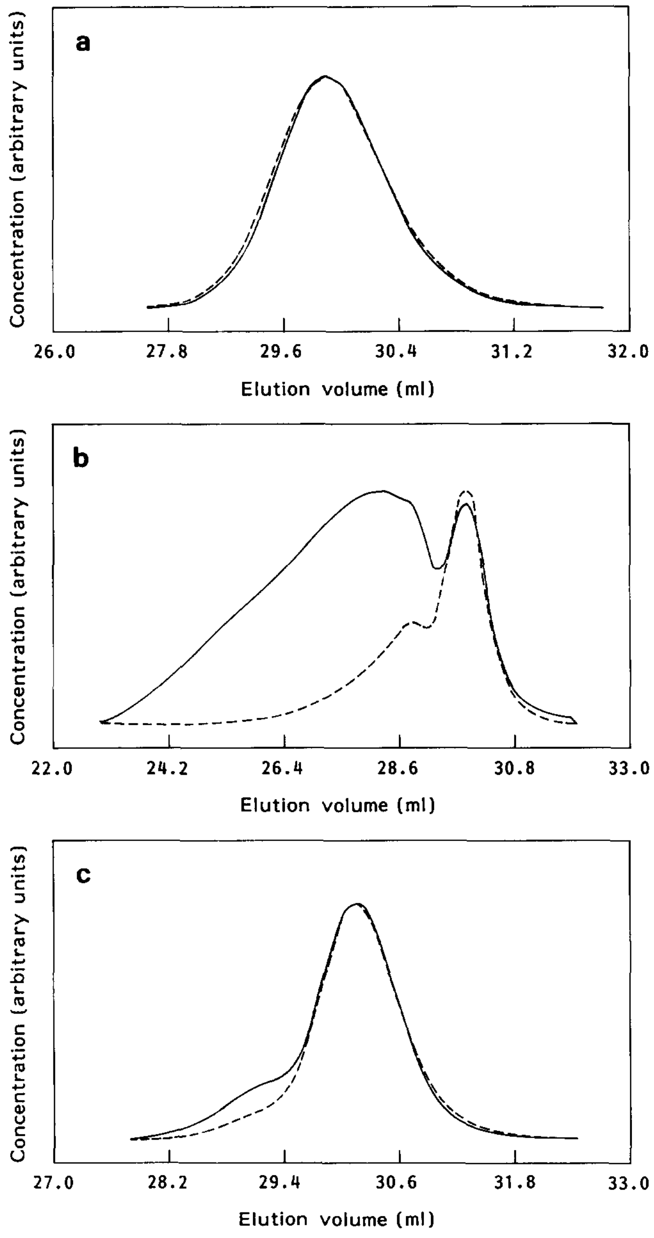


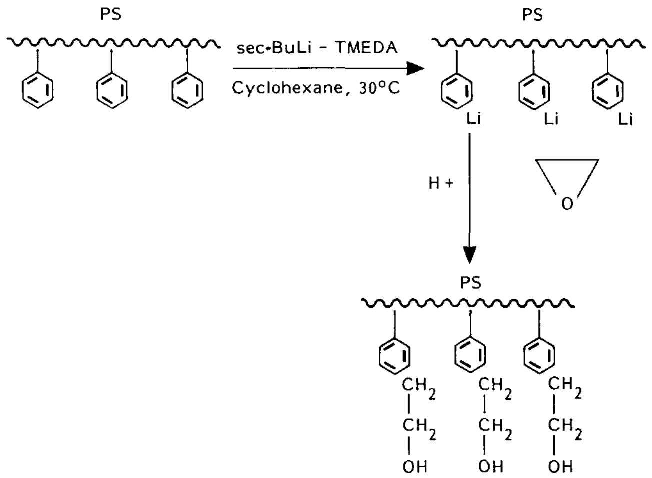
Figure 2 S.e.c. chromatograms of polystyrene before functionalization (a) and after functionalization using 27 × 10^{-3} mol sec-butyllithium (b) and linear fraction of functionalized polystyrene (c): (——) light scattering detection; (- - -) refractometric and u.v. detections

Table 2 Characteristics of statistically hydroxylated polystyrenes

Sample[a]	$\bar{M}_w$[b]	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$	N(OH)[c]
UPS	53 300	53 000	1.01	
PSA	173 000	90 000	1.92	12
PSB	78 000	65 000	1.20	6

[a] UPS, linear polystyrene precursor; PSA, UPS reacted with 27 × 10^{-3} mol sec-butyllithium; PSB, UPS reacted with 13 × 10^{-3} mol sec-butyllithium
[b] Determined by s.e.c.-LALLS (g mol^{-1})
[c] Expected number of OH groups per chain

method can be summarized by the following reaction scheme:



Statistical metallation on the polystyrene phenyl groups is achieved in a first step through the action of sec-butyllithium, in the presence of TMEDA. The reaction with ethylene oxide and subsequent addition of acetic acid yields the expected polymer with pendent hydroxyethyl functions. The characteristics of the unmodified polymer (UPS) and of the polymer samples obtained after functionalization using, respectively, 27 × 10^{-3} and 13 × 10^{-3} mol sec-butyllithium (PSA and PSB) are summarized in *Table 2*. The corresponding s.e.c. curves are shown in *Figures 2b* and *3b*. A first observation concerns the average molecular weights of the functionalized samples and their distribution. Instead of a very slight increase due to the introduction of the

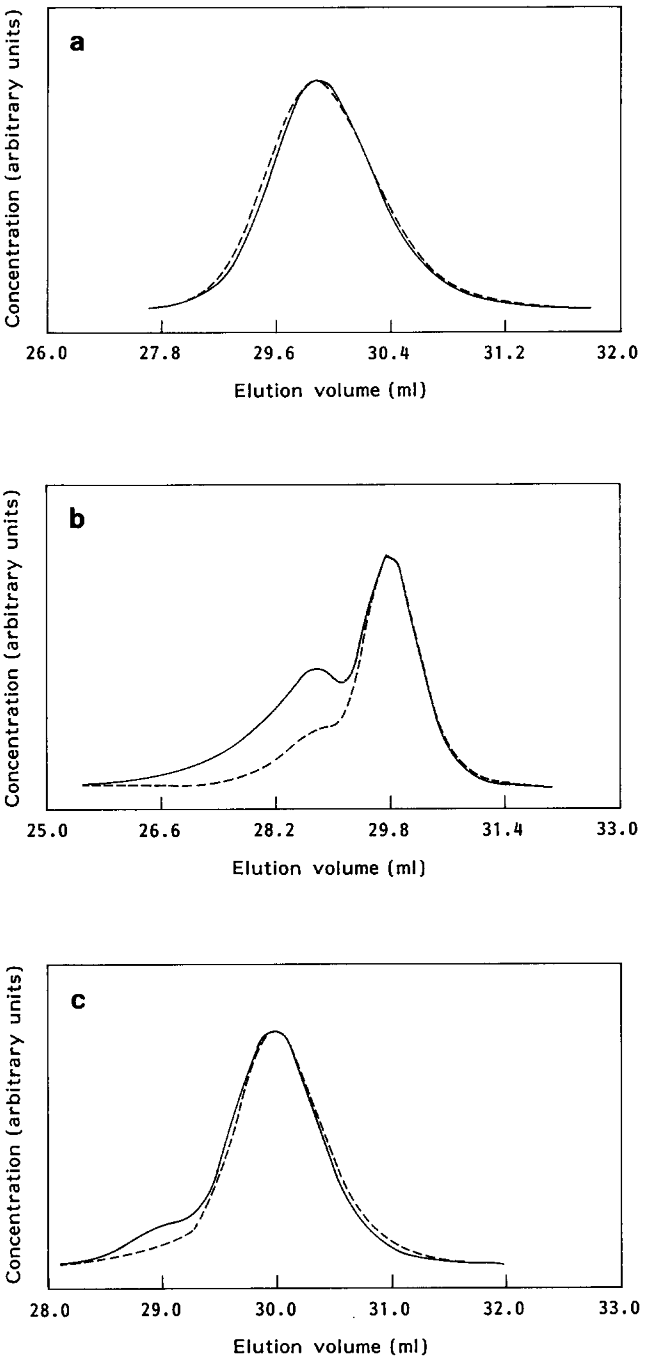


Figure 3 S.e.c. chromatograms of polystyrene before functionalization (a) and after functionalization using 13×10^{-3} mol sec-butyllithium (b) and linear fraction of functionalized polystyrene (c): (——) light scattering detection; (- - -) refractometric and u.v. detections

functional groups (below experimental accuracy), a noticeable increase is observed with a broadening of the distribution. The larger the amount of sec-butyllithium used for metallation, the more pronounced is this effect. The s.e.c. curves show one maximum which corresponds to the initial molecular weight and in addition a second maximum in the higher molecular weight range. With light scattering detection the latter is strongly increased, an indication that higher molecular weight, branched species are present, as a result of an intramolecular side reaction. Several attempts to avoid their formation, in changing the experimental conditions, did not succeed. Such a phenomenon was not mentioned in earlier work reported in the literature. The nature of the reaction responsible for branching has not yet been established. It was checked, however, that it does not take place in the course of the metallation process. Indeed, when the metallated phenyl units of the polystyrene are protonated by addition of methanol or acetic acid, the initial polymer is recovered, without any trace of higher molecular weight species. Thus branching occurs in the second step, after addition of ethylene oxide. An investigation on a model system, which will be published in a coming paper, is presently in progress. A first analysis of these experiments indicates that, indeed, in addition to the expected main reaction, complex side reactions occur. There is evidence that among them exists the formation of a linkage between phenyl groups, although to a rather low extent, but which could explain chain branching.

Since the functional precursor polystyrene to be used in further investigations had to be linear, branched and linear species had to be separated by fractionation. *Table 3* gives the characteristics of the recovered linear polymers and the average values corresponding to the fraction of branched polymer. It is worth noting that the molecular weights of the linear polymer are quite close to those of the initial polystyrene. *Figures 2c* and *3c* show the s.e.c. curves of the linear fractions PSA and PSB. Only traces of branched molecules remain in these samples. They are not apparent on the refractometric curve, but their presence is still visible by light scattering detection. However they are responsible for the somewhat higher average molecular weights of these fractions in comparison with the unmodified polymer UPS. The molecular weight of the branched molecules is not very high, thus their degree of branching should be low, which implies that the contribution of the side reaction is rather limited.

Table 3 also displays the number of hydroxyethyl groups per polymer chain and the average molecular

Table 3 Characteristics of fractionated statistically hydroxylated polystyrenes

Sample	$\bar{M}_w{}^a$	$\bar{M}_n{}^a$	$\bar{M}_w/\bar{M}_n$	$N_{OH}^{u.v.\,b}$	$\bar{M}_{ch}^{u.v.\,b}$	OH^c (%)	$N_{OH}^{Ph\,d}$	$\bar{M}_{ch}^{Ph\,d}$
PSA	61 000	59 000	1.03			0.375	13.8	4300
PSAR	194 000	97 000	2.00					
PSB	60 200	58 200	1.03			0.240	5.5	6700
PSBR	110 000	84 200	1.31					
PSAN	65 000	63 000	1.03	8.1	7800			
PSBN	61 000	59 000	1.03	4.2	14 000			

[a] Determined by s.e.c.-LALLS (g mol^{-1})
[b] Number of OH functions determined by u.v. spectroscopy and molecular weight of chain segments between functional units
[c] Determined by phosgenation titration
[d] Number of OH functions given by phosgenation titration and molecular weight of chain segments between functional units

weight of the chain segments between the pendent functions. For comparison we have indicated both the values obtained by u.v. spectrometry and by the phosgenation method. Again, the number of hydroxyl functions determined by the second method is noticeably higher. It can be considered as erroneous: according to the previous observations on the α,ω-difunctional polystyrene, it is overestimated.

The modified polystyrenes have functionalities lower than expected from preliminary experiments. Thus the metallation method cannot be reproduced quantitatively and only an approximate prediction of the degree of functionalization is possible. However in the present case it does not represent a major drawback.

CONCLUSIONS

The purpose of this paper was to prepare well defined functional polystyrenes fitted with hydroxyethyl groups at chain ends or as pendent functions, statistically distributed along the polymer backbone. The first type of polystyrene was prepared by anionic polymerization, followed by endcapping of the anionic chain ends, which is the best way to obtain an α,ω-difunctional polymer with well defined characteristics. Samples with a given molecular weight and fitted with pendent groups were prepared by modification of a precursor polymer with the desired molecular characteristics. The method requires two steps: creation of metallated sites along the polymer chain, followed by reaction with ethylene oxide and protonation to yield hydroxyethyl groups. Different degrees of metallation, depending upon the amount of metallating agent used, can be obtained. In this case fractionation of the product is necessary to separate the linear polymer from branched species formed in the second step. The number of hydroxyl functions per chain for these samples can be determined quite accurately by u.v. spectrometry after labelling.

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