Study of two-step capping in the synthesis of epoxy-terminated polystyrene oligomers by acid–base titration and gel permeation chromatography

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The synthesis of epoxy-terminated polystyrene was studied by high performance gel permeation chromatography and titration of sodium hydroxide in the presence of hydrochloric acid. The effect of the terminated reaction was also studied. The introduction of an end-capping reagent, cyclosulphide propane, had a retarding effect on the side reaction, whereas ring opening substances had an end-capping effect linking with carbanionic living polystyrene. The properties of the products would be expected to differ from those of the oligomers without capping, because carbanionic living polystyrene promotes thermal stability rather than an end-capping reagent character; this was deduced by acid–base titration and gel permeation chromatographic analysis in tetrahydrofuran.

(Keywords: synthesis; macromer; gel permeation chromatography)

INTRODUCTION

Living oligomers or polymers may resume their growth whenever monomer is added to the system. This, indeed, is the most versatile technique for synthesizing block polymers and graft polymers[1–4]. Epoxy-terminated polystyrene is a living oligomer, which possesses active, growth sustaining end-groups on one end[5]. Epoxy is a functional end-group. A logical extension of molecular weight (MW) control/end-group functionalization is the preparation of functionally terminated oligomers possessing reactive end-groups. Their molecular weights are generally from 5×10^2 to 2×10^4 ($g\,mol^{-1}$)[6,7]. A two-step capping approach is found suitable for higher concentrations of living oligomers.

The carbanionic living polystyrene was capped with cyclosulphide propane, converting the end-group into sulphide propane. The concentration of the latter was determined by spectroscopy and the epoxy end-group was determined by acid–base titration in order to disclose the presence of epoxy groups present after treating with cyclosulphide propane. The agent used in the titration must react irreversibly and quantitatively with living polymers, but not with dead ones. Since the epoxide reacts with hydrochloric acid to form a chlorohydrin, the amount of hydrochloric acid unconsumed was determined by titration with a standard base. The end-point is determined by the appreciable violet colour in some convenient property of the system, e.g. by the disappearance of the colour of living polymers, provided that the dead polymers are colourless.

A number of investigations have been carried out on the determination of molecular weights and MW distributions of polymers[8–12]. In this article we study the synthesis of epoxy- and sulphide propane-terminated polystyrene in the presence of some organic substances, such as cyclohexane. The effect of various organic substances on the rate of synthesis, obtained average molecular weights, molecular weight distribution (MWD) and concentration of living oligomers was determined by acid–base titration and gel permeation chromatography.

EXPERIMENTAL

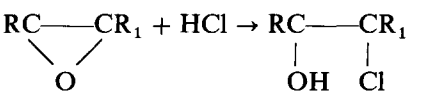
Apparatus and materials

The concentrations of epoxy terminated polystyrene oligomers (Ps-ep) were determined by acid–base titration. Ps-ep oligomers were dissolved in a mixture of hydrochloric acid and dioxane, and titrated with a standard solution of 0.1 N NaOH in ethanol.

Gel permeation chromatographic analysis was performed on a Shimadzu LC-4A chromatograph equipped with Microstyragel columns (10^5, 10^4, 10^3 and 500 Å), a spectrophotometer, Chromatopac C-R2AX, and tetrahydrofuran (THF) as solvent. The columns were calibrated with polystyrene standards. A viscometer was used to determine the intrinsic viscosity (η) of Ps-ep oligomers.

Analysis of the epoxy end-group of oligomers

Hydrochlorination methods. The epoxides react with hydrochloric acid, forming a chlorohydrin:



The difference between the amount of acid added and

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the amount unconsumed, as determined by titration with a standard base, is a measure of the epoxide[13].

Procedures: 2 g of oligomer was added to a 250 cm^3 flask into which 25 cm^3 of 0.2 N hydrochlorination reagent had been pipetted. The mixture was shaken and maintained for 2 h at 30°C. Several drops of 0.1% cresol red indicator solution and 25 cm^3 of anhydrous ethanol were added, and the excess of acid was titrated with standard methanolic 0.1 N sodium hydroxide solution to the first violet colour of the end point. A control was run under identical conditions.

Calculations:

$$\% \text{ Ps-ep oligomers} = \frac{(V_1 - V_2) \times N \times M_n}{1000 \times \text{weight of sample}} \times 100$$

where V_1 = cm^3 of sodium hydroxide solution required for the control; V_2 = cm^3 of sodium hydroxide solution corresponding to the excess acid solution; M_n = number molecular weight of Ps-ep oligomer; N = normality of standard sodium hydroxide solution.

Characterization of molecular weight and MW distribution

Determination of molecular weight and MW distribution was carried out by gel permeation chromatography in THF at ambient temperature using Shimadzu microstyragel columns and a spectrophotometer as detector at 262 nm. The system was calibrated with polystyrene standards having polydispersities close to unity, which were supplied by Shimadzu Corporation (Kyoto, Japan). The molecular weights of the oligomers were determined from a universal calibration method and Mark–Houwink–Sakurada constants K and α for polystyrene and oligomers in THF at room temperature. Molecular weight averages and polydispersities were defined in the conventional fashion[14–16].

Membrane osmometry, an absolute method for determination of number average molecular weight, was used to confirm the size exclusion chromatography results. The oligomers in toluene were run on a membrane osmometer made in China.

Determination of constants $K\eta$ and α

Gel-permeation chromatography (g.p.c.) may be used to determine the degree of swelling of polymers in solution and the shape of their macromolecules. These properties are characterized to a certain extent by the constants α and $K\eta$ in the Mark–Kuhn–Houwink equation: $[\eta] = K\eta \times M^{\alpha}$. Gel permeation chromatography makes it possible to determine these constants[17,18]. The values of $[\eta]$ for each sample are measured with a viscometer and the difference free energy $\tilde{\varepsilon}_i$ of the chain, which should now be considered to be a function of $K\eta$ and α, is derived. One should find the minimum of the function of two variables $\sum_{i=1}^{m} \tilde{\varepsilon}_i(K\eta, \alpha)$ for the segments of the macromolecule. The chromatographic system is characterized by the universal calibration dependence, so one can write it in the general form:

$$\ln(M[\eta]) = f(V) \qquad (1)$$

Universal calibration (1) permits the determination of the constants α and $K\eta$ if only one oligomer sample is available. For this purpose it is sufficient to obtain its chromatogram and to determine by independent methods any two of its three average characteristics: $[\eta]$, M_w or M_n. When they are known, it is possible to write the following system of equations:

$$[\eta] = \frac{1}{S} K\eta \frac{1}{(\alpha+1)} \int_{V_1}^{V_2} \exp\left[\frac{\alpha}{\alpha+1} f(V)\right] F(V)\,dV$$

$$M_w = \frac{1}{S} K\eta - \frac{1}{(\alpha+1)} \int_{V_1}^{V_2} \exp\left[\frac{\alpha}{\alpha+1} f(V)\right] F(V)\,dV \qquad (2)$$

$$M_n^{-1} = \frac{1}{S} K\eta \frac{1}{(\alpha+1)} \int_{V_1}^{V_2} \exp\left[-\frac{1}{\alpha+1} f(V)\right] F(V)\,dV$$

where S is the selectivity, defined as the relative difference between retention volume of the two components being separated; V_1 and V_2 are the elution volumes limiting the chromatogram; $F(V)$ is a function of retention volume; and $f(V)$ is equal to $\ln(M[\eta])$. The left-hand side of equation (2) contains values found from viscometric and osmometric data and the right-hand side contains those found from chromatographic experiment by using the chromatogram of the sample and the parameters of universal calibration. Evidently, from a combination of any two equations of system (2) the constants $K\eta$ and α of the oligomers can have the following values:

$$K\eta = 1.80 \times 10^{-4} \qquad \alpha = 0.73$$

Linear calibration of Ps-ep oligomers is as follows:

$$\text{Log } M = 7.681 - 0.324V_e \qquad \text{(THF, 25°C)}$$

RESULTS AND DISCUSSION

Characterization of reaction mechanism

The synthesis of Ps-ep oligomers is described by the mechanism:

$$\text{n-BuLi} + n\ \text{st} \rightarrow \text{n-Bu(st)}_n^{\ominus}\text{Li}^{\oplus}$$

$$\text{n-Bu(st)}_n^{\ominus}\text{Li}^{\oplus} + \text{Cl–CH}_2\text{CH}\!-\!\!-\!\text{CH}_2 \rightarrow \text{n-Bu(st)}_n\text{CH}_2\text{CH}\!-\!\!-\!\text{CH}_2 + \text{LiCl}$$

(O)

In this system most living polymers are in a dormant form and only a small but active fraction of them contributes to propagation. For example, more than 95% of living polymers could form the rather unreactive ion-pair, lithium polystyrene salt, while a low percentage is present as the highly reactive free ions that are responsible for the observed propagation. It is due to aggregated lithium polystyrene salt is inert in hydrocarbon medium, and only a small fraction of the non-aggregated salt propagates the observed polymerization, spectroscopy informs about a little capped species.

Figure 1 shows two peaks containing three kinds of substances: $(Ps)_2$ dimers, Ps homopolymer and Ps-ep oligomers. The components represented by peaks (I) and (II) were obtained by g.p.c. and the concentration of Ps-ep oligomers was determined by hydrochlorination methods; therefore peak (I) was defined as $(Ps)_2$ dimers according to their molecular weight, and peak (II) was associated with Ps homopolymers and Ps-ep oligomers.

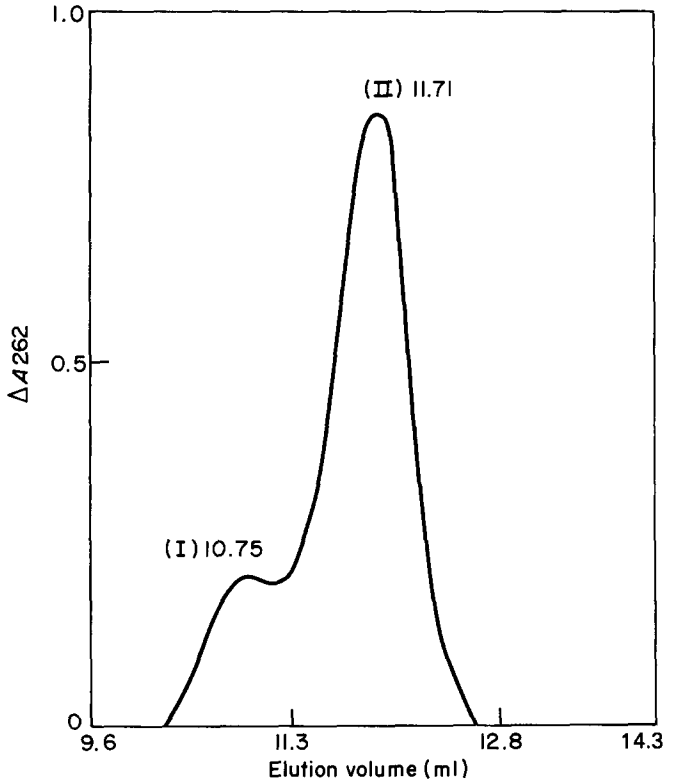


Figure 1 Gel permeation chromatogram of products from terminal reaction between $PS^{\ominus}Li^{\oplus}$ and $ClCH_2CH\text{—}CH_2$ (O)

It is known from the titration analysis that epoxy groups were reduced in the end-reaction with propylchloride epoxy and therefore its product exists in two forms of cyclization and linearity. This implies the following mechanism of terminal reaction.

$$Ps^{\ominus}Li^{\oplus} + Cl\text{–}CH_2CH\text{—}CH_2 \;(O) \rightarrow Ps\text{–}CH_2\text{–}CH\text{—}CH_2\;(O) + LiCl$$

Rather different side reactions take place in the terminal reaction of carbanionic living polystyrene, causing, e.g. ring opening:

$$Ps^{\ominus}Li^{\oplus} + Cl\text{–}CH_2CH\text{—}CH_2\;(O) \rightarrow Ps\text{–}CH_2\text{–}CH(OLi)\text{–}CH_2Cl$$

or coupling:

$$Ps^{\ominus}Li^{\oplus} + Cl\text{–}CH_2\text{–}CH(OLi)\text{–}CH_2\text{–}Ps \rightarrow Ps\text{–}CH_2\text{–}CH(OLi)\text{–}CH_2\text{–}Ps + LiCl$$

$$Ps^{\ominus}Li^{\oplus} + CH_2\text{–}CH\text{–}CH_2\text{–}Ps\;(O) \rightarrow Ps\text{–}CH_2\text{–}CH(OLi)\text{–}CH_2\text{–}Ps$$

The carbanionic living polystyrene is combined not only with carbon atoms linking chlorine in a nucleophilic reaction of the anion $Ps^{\ominus}$ and epoxide but also with one linking oxygen on ring opening of the epoxy. On the other hand, the epoxides present in both reactions of substituting chlorine and ring opening of the epoxy so that Ps-ep oligomers were obtained with difficulty.

Effect of end-group

The carbanionic living polystyrene was reacted with propylchloride epoxy (CE), propylbromide epoxy (BE) and propyliodide epoxy (IE) in a thermal reaction. The experimental results of three different concentrations of Ps-ep oligomers are given in *Table 1* and *Figure 2*. Propylchloride epoxy is the most efficient agent for the highest concentration of 77.8% Ps-ep oligomers. We have found the capping reaction of the carbanionic living polystyrene with alkylhalide was in opposition to organic chemistry on the substitution order of nucleophilic

Table 1 Effect of endgroup

Sample no.	End group	$M_n \times 10^{-3}$	Ps-ep (%)
I	CE	6.7	77.8
II	BE	6.7	19.47
III	IE	6.7	0

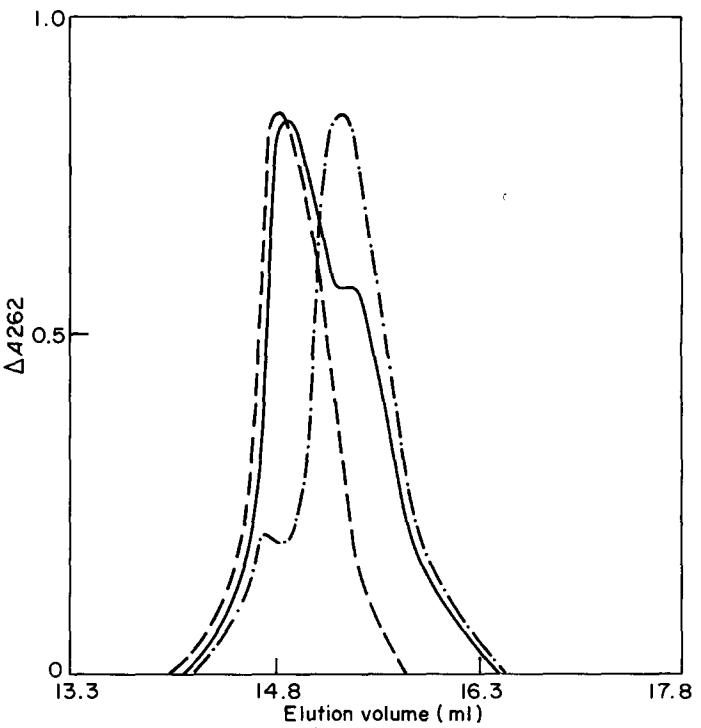
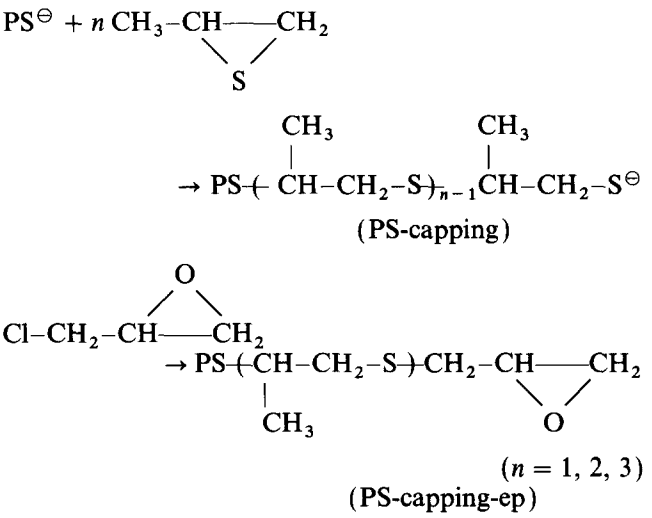


Figure 2 Typical g.p.c. curves of the epoxy terminated polystyrene oligomers run in THF at 30°C and 1 cm min^{-1}: –·–·–, $PS^{\ominus}$ + CE; ——, $PS^{\ominus}$ + BE; – – –, $PS^{\ominus}$ + IE

reactions. The carbanionic living polystyrene combined easily with carbon atoms linking chlorine since the atomic volume of chlorine is the smallest of the three halide atoms due to their positional resistances.

Effect of end-capping reagent

The carbanionic living polystyrene was capped with cyclosulphide propane, then terminated with epoxy end-groups as follows:



(PS-capping)

(PS-capping-ep)

The two-step terminal reaction produces a higher concentration of Ps-ep oligomers than the one-step reaction shown in *Table 2*. Sulphides are more easily produced in the substitution reaction presented by the SN2 mechanism than carbanion because the geometry resistance of the nucleophile is presented in the adjacent benzene ring of carbanion. The molecular weight and MW distribution of Ps-capping-ep oligomers are very different from Ps-ep oligomers according to g.p.c. analysis.

Effect of solvent

The oligomers were prepared with three kinds of solvent. As shown in *Table 3*, the end group concentrations of Ps-ep oligomers are very different in different solvents. A high concentration of 81.6% Ps-ep

Table 2 Effect of end-capping reagent

Sample no.	$M_n \times 10^{-3}$	Two kinds of terminated reaction	Ps-ep (%)
A1	5.8	$PSCHCH_2S^{\ominus} + CE$ (with CH_3)	76.8
A2	5.8	$PS^{\ominus} + ClCH_2CH\text{—}CH_2$ (O)	47.9
B1	7.6	$PSCHCH_2S^{\ominus} + CE$ (with CH_3)	80.2
B2	7.6	$PS^{\ominus} + ClCH_2CH\text{—}CH_2$ (O)	59.8
C1	9.8	$PSCHCH_2S^{\ominus} + CE$ (with CH_3)	82.5
C2	9.8	$PS^{\ominus} + ClCH_2CH\text{—}CH_2$ (O)	61.7

Table 3 Effect of solvent

Sample no.	Solvent	$M_n \times 10^{-3}$	Ps-ep (%)
1	Toluene	6.51	78.9
2	Cyclohexane	6.51	81.6
3	Benzene	6.51	55.2

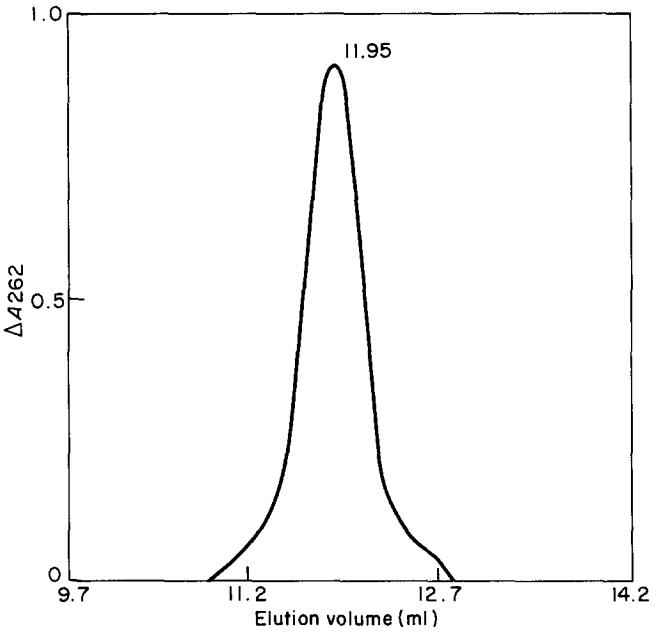
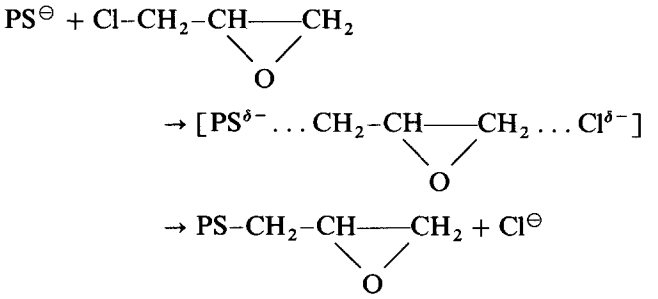


Figure 3 Gel permeation chromatogram of products from terminated reaction ($PS^{\ominus}$ + CE) in toluene solvent

Table 4 Effect of temperature

Sample no.	$M_n \times 10^{-3}$	Temperature (°C)	Ps-ep (%)
1	8.7	50	65.9
2	8.7	45	70.5
3	8.7	30	72.8
4	8.7	24	82.1
5	8.7	0	83.2

oligomers was obtained in cyclohexane solvent because cyclohexane has weaker polarity than the other two solvents. The carbanionic living polystyrene is terminated by epoxy end-groups which are fitted to the SN2 mechanism of the substitution reaction of the nucleophile.



A successful example of this view is that the stability of transition states is decreased with increasing polarity of solvent because of the dispersion of their electrical charges. The chromatogram in *Figure 3* shows that there

Table 5 Interdependence of MW and MWD and macromers

Sample no.	Ps-ep oligomers			Ps-ps homopolymers		
	$M_n \times 10^{-3}$	M_w/M_n	Concentration (%)	$M_n \times 10^{-3}$	M_w/M_n	Concentration (%)
1	2.2	1.15	68.3	6.3	1.05	31.7
2	2.8	1.10	66.9	7.6	1.05	33.3
3	4.2	1.09	68.6	11.2	1.04	31.4
4	5.6	1.09	76.2	14.6	1.04	23.8
5	6.1	1.09	78.7	15.8	1.04	21.3
6	6.9	1.08	79.3	17.4	1.04	20.7
7	8.6	1.08	82.2	21.3	1.04	17.8
8	8.8	1.08	79.9	21.9	1.04	20.1
9	9.8	1.08	82.6	24.5	1.04	17.4
10	10.3	1.08	80.9	25.7	1.04	19.1
11	11.6	1.08	82.8	28.8	1.04	17.2

are no $(PS)_2$ dimers, only Ps-ep oligomers and PS homopolymers. These can be used to produce active hydrogen protons with reactive solvents. Finally, we also find that the living end species can be converted into dead ones with a spontaneous reaction.

Effect of temperature

The concentration of Ps-ep oligomers formed at equilibrium changes with temperature. The experimental results in *Table 4* show that the concentration of Ps-ep oligomers in the product increases with decreasing temperature. The activation energy of the terminal reaction is different from that of ring opening for epoxy. On the other hand, the active groups on carbanionic living polystyrene protrude less from the chain and are more crowded so that the nucleophile attacks the epoxide with difficulty. Of course, the solution properties of living polystyrene have a little chance to be contracted closely by out-rule one. Hence the rate of terminal reaction of carbanionic living polystyrene may be greatly affected by shifts in the relative equilibria caused by thermodynamics.

Effect of molecular weight and MW distribution

Table 5 shows that the concentration of Ps-ep oligomers changes little when the molecular weight is between 5.6×10^3 and 11.6×10^3, the concentration being between 76.2% and 82.8%. The concentration of Ps-ep oligomers decreases with decreasing molecular weight. It seems that both living polystyrenes are easily coupled into $(PS)_2$ dimers between molecules having small molecular weight because the epoxy end-group can be converted into a linear end-group.

The molecular weight distribution of Ps-ep oligomers shows a narrow dispersion ($M_w/M_n = 1.08 \sim 1.09$) in the above-mentioned range of molecular weights but it widens little with reducing molecular weight. The reason is that the resistance among the molecules is increased with the growing thermal movement of the molecules; however, this situation is favourable to forming Ps-ep oligomers.

CONCLUSIONS

Acid–base titration and g.p.c. analysis of the living oligomer was carried out to investigate epoxy functionally terminated polystyrene oligomers with capping in two steps. A quantitative end-group functionalization with aliphatic epoxy groups via a novel end-capping reagent, cyclosulphide propane favoured increase of the concentration of living oligomers.

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