Living anionic synthesis and characterization of poly(epichlorohydrin-*g*-styrene) copolymers

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Poly(epichlorohydrin-*g*-styrene) copolymers, P(ECH-*g*-S), of a wide range of compositions have been prepared in an argon atmosphere by coupling or deactivation of living polystyrene anions, PS^-, at the chloromethyl groups of polyepichlorohydrin, PECH, in solution in benzene, C_6H_6, toluene, CH_3–C_6H_5, tetrahydrofuran, THF, and C_6H_6–THF solvent mixtures, usually at 20°C. When both polystyryl lithium, PS^-Li^+, and PECH were in C_6H_6 or toluene, grafting reactions were accompanied by cross-linking due to lithium–halogen interchange, colloidal phase separation and degradation of the backbone polymer. When the PS^-Li^+ in either C_6H_6 or THF was coupled with PECH in THF, cross-linking was avoided and degradation was minimized. Some non-degradative termination reactions also occurred on coupling in THF and THF–C_6H_6 mixtures. A polar solvent was, however, found to be favourable for the coupling reaction. The graft copolymers were purified by fractional precipitation techniques and were characterized by infra-red spectroscopy, ultraviolet spectroscopy, microanalysis, gel permeation chromatography and solubility.

INTRODUCTION

Epichlorohydrin (ECH) elastomers including the homopolymer, polyepichlorohydrin, PECH and the 1:1 molar ratio copolymer with ethylene oxide, designated P(ECH-co-EO), are notable for their good balance of physical and chemical properties[1,2]. These two elastomers are now manufactured for example, by Hercules and Goodrich in America.

Epichlorohydrin polymers contain pendant $-CH_2Cl$ groups which are reactive towards nucleophilic reagents. Various modifications of the polymers involving nucleophilic substitution of –Cl by other groups, such as hydroxyl[1,3,4] have been achieved. In such substitutions, polymer degradation may also occur in the presence of either strong bases or poor nucleophiles[5].

Various graft copolymers of ECH elastomers have been prepared, mostly by free-radical methods. These methods include the use of organic peroxide initiators[6-8], use of transition metal-labile ligand complex catalysts[9-11] and the polymer hydroperoxide[12].

The synthesis of graft copolymers from polymeric halides by the cationic initiation technique, particularly developed by Kennedy[13,14] is most suitable for polymers containing tertiary or allylic halogen atoms and hence has not yet been applied by ECH polymers. Cationic polymerization of styrene in the presence of PECH, using boron trifluoride etherate as catalyst, led to the formation of ECH–styrene copolymers rather than well-defined graft copolymers[15].

The grafting of ECH polymers by nucleophilic attack on $-CH_2Cl$ groups, by the carbanionic coupling technique[16,17], has, however, received little attention, and experimental evidence is limited[18]. This paper describes the synthesis of P(ECH–g–S) copolymer by carbanionic coupling and an investigation of some of the degradative side reactions accompanying the grafting reactions.

EXPERIMENTAL

Reagents and purification

n-Butyl lithium. n-BuLi (Alpha Products), supplied as a 2.5M solution in n-hexane was diluted with purified n-hexane to an approximately 0.5M solution. The resulting solution was analysed by the 'double titration' method of Gilman and Haubin[19]. The reagent was used as an initiator for the anionic polymerization of styrene in benzene and toluene.

Cumyl potassium. Cumyl-K (Orgmet Inc., Hamstead, N.H., U.S.A.), supplied as a suspension in n-heptane in the presence of excess metallic potassium, was diluted with purified THF, and filtered under high purity-grade argon to remove potassium. The reagent was stored under argon in a sealed ampoule at −20°C to prevent any slow reaction of cumyl-K with THF and was used as initiator for polymerization of styrene in THF. The concentration of cumyl potassium was estimated by a method based on the reaction of cumyl-K with n-butyl bromide to form potassium bromide which was estimated by silver nitrate titration[20].

Benzene. (Koch-Light Laboratories Ltd.) was first dried over powdered calcium hydride, CaH_2, and fractionally distilled. The middle fraction distilling at 79°–80°C (1 atmosphere) was again dried over living polystyryl lithium on the vacuum line and finally distilled under vacuum into the polymerization flask.

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Toluene. (Koch-Light Laboratories Ltd.) was initially dried over powdered CaH_2 and then fractionally distilled. The middle fraction distilling at 110°C (1 atmosphere) was dried over Na/K alloy on the vacuum line and distilled directly into the polymerization flask.

Tetrahydrofuran., THF, (Hopkins and Williams) was first dried over Linde 4A molecular sieve, then over powdered CaH_2 and was finally fractionally distilled. The middle fraction distilling at 64°–66°C (1 atmosphere) was dried over Na/K alloy on the vacuum line and then distilled into the polymerization flask, or ampoules which were later sealed off under vacuum.

Styrene (BDH), as supplied contained 0.001–0.002% w/v tertbutyl catechol as stabilizer. It was dried over powdered CaH_2 and then fractionally distilled under reduced pressure. The middle fraction distilling at 60°–62°C (40–42 mm pressure) was stored over fresh powdered CaH_2. It was twice distilled from this drying agent in the vacuum line before direct distillation into the storage ampoules.

n-Hexane (BDH), used for dilution of n-BuLi, was dried over powdered CaH_2 and then fractionally distilled. The middle fraction distilling at 67°–68°C (1 atmosphere) was dried with n-BuLi and distilled on the vacuum line before use.

Benzyl Chloride (Hopkin and Williams) used for the estimation of n-BuLi concentration, was dried over phosphorus pentoxide, P_2O_5, and distilled in the vacuum line before use.

n-Butylbromide (BDH) used for the estimation of cumyl-K concentration was dried over fused $CaCl_2$ and distilled. The distillate coming out at 101°–102°C (1 atmosphere) was dried over P_2O_5 and redistilled on the vacuum line before use.

Methanol (AR, BDH), MeOH, used for the termination of living polymer was degassed with argon. The reagent used for purification of polymers was technical grade (BDH).

Argon (British Oxygen Co.), 99.998 v/v was passed through activated silica gel before use.

Polyepichlorohydrin, PECH, used as backbone polymer was obtained by rough fractional precipitation of 'Herchlor H' (Hercules Inc.) from a 2% w/v benzene solution with methanol. The middle fraction was retained and was reprecipitated similarly in a Waring blender. This polymer, freed from antioxidant, was dried to constant weight in a vacuum oven at 45°C and stored in a vacuum desiccator in the dark before use, in order to minimize oxidative degradation. The oxidative degradation of PECH induced by u.v. light will be discussed in a subsequent paper.

Topanol CA (ICI Ltd), 1,1,3-tris (2-methyl-4-hydroxy-5-t-butyl phenyl) butane, was used as an antioxidant (0.1% w/v solution in MeOH) in precipitation of all PECH and P(ECH-*g*-S) samples.

Chloroform (BDH), spectroscopic grade, was used as a solvent for u.v. analysis of the polymer samples.

Characterization

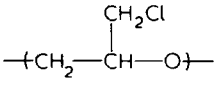
Gel permeation chromatography, g.p.c. G.p.c. measurements were carried out by the Polymer Supply and Characterization Centre, RAPRA, Shawbury, Shrewsbury, using 0.2% w/v solutions of polymers in THF at 20°C. Differential molecular weight distribution curves, *MWD* curves, were plotted using the g.p.c. traces.

Infra-red, i.r. I.r. measurements of the purified polymer samples were made using a Perkin-Elmer 157G Grating Spectrophotometer, using thin films of polystyrene, PS, PECH and P(ECH-*g*-S) samples directly cast onto NaCl plates from methylene chloride or chloroform solutions.

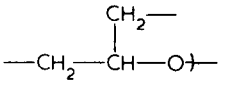
Ultraviolet, u.v., and graft copolymer composition. U.v. spectra of polymer samples, freed from antioxidant, were recorded in spectroscopic grade chloroform solutions, using a Perkin-Elmer 137UV spectrophotometer. Measurements at 262 nm were used to determine the specific extinction coefficients of a P(ECH-*g*-S) sample, E^*_{graft}, expressed in $dm^3\ g^{-1}\ cm^{-1}$. In separate experiments using homopolymers, the specific extinction coefficients for PECH, E^*_{PECH}, and for PS, E^*_{PS}, were measured. Hence the weight fraction of PS in the graft copolymer, y, was calculated using the equation[21]:

$$E^*_{graft} = y\,E^*_{PS} + (1-y)\,E^*_{PECH}$$

From the value of y for a given graft copolymer, the % PS (w/w) and the % PECH (w/w) may be calculated, where the % weight PECH includes both the unsubstituted,



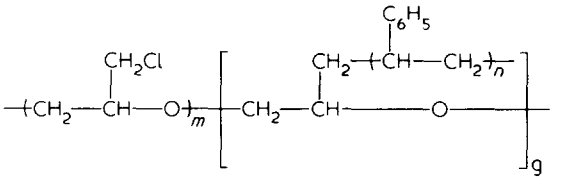
and substituted,



ether repeat units, and % PECH = 100 − % PS. Spectra of at least three solutions at different concentrations were recorded for each polymer sample, and values of each specific extinction coefficient were calculated from the slope of the plot of absorbance at 262 nm, an absorbance maximum for polystyrene, against concentration.

Elemental microanalysis and graft copolymer composition. Elemental microanalysis of samples of PECH and P(ECH-*g*-S) were carried out for carbon, hydrogen and chlorine.

The general formula of a graft copolymer may be represented:



The % chlorine in a given graft copolymer, together with the molecular weight of the PS grafts, $\bar{M}_n$(PS), measured separately as described later, were used to determine copolymer compositions. From the % chlorine, %Cl, the value of (m/g) for a given graft copolymer may be calculated, using:

$$\%Cl = \left(\frac{35.45m}{92.53m + 104.15ng + 57.07g}\right) \times 100$$

$$= \left(\frac{35.45\,(m/g)}{92.53\,(m/g) + \bar{M}_n(\mathrm{PS}) + 57.07}\right) \times 100$$

Then, the %PECH may be evaluated using the equation:

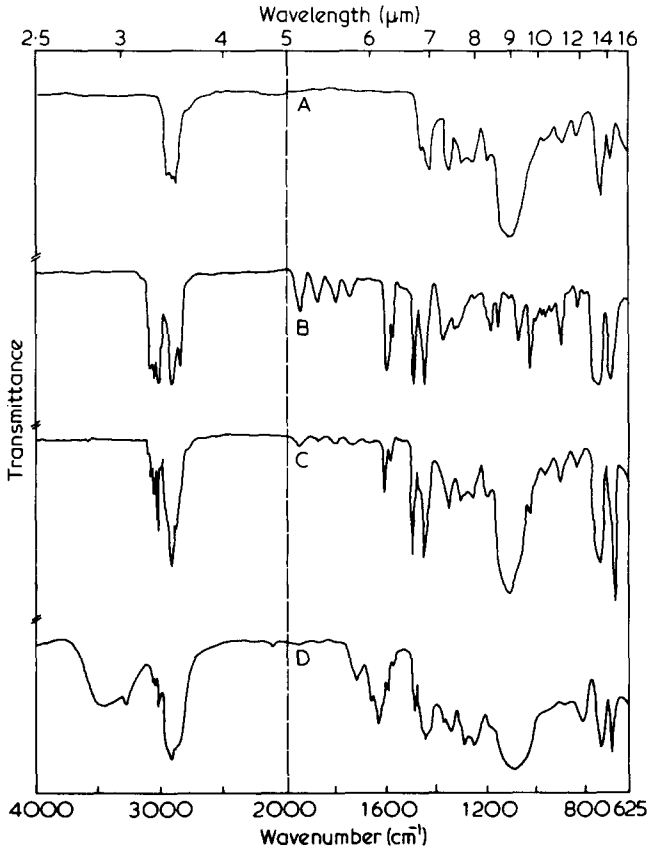


Figure 1 Infra-red spectra: (A), a sample of amorphous polyepichlorohydrin; (B), a sample of polystyrene prepared anionically; (C), poly(epichlorohydrin-*g*-styrene) sample G5–G, containing 47% w/w polystyrene; (D), methanol soluble degraded graft copolymer sample G1 A

$$\%\text{PECH} = \left(\frac{92.53\,(m/g) + 57.07}{92.53\,(m/g) + \bar{M}_n(\text{PS}) + 57.07} \right) \times 100$$

Turbidimetric titration

Turbidimetric titrations of impure P(ECH-*g*-S) samples mixed with homopolystyrene as well as that of separate homopolystyrene samples were performed using a Model 49 EEL spectrophotometer in conjunction with a type 200 EEL galvanometer connected to the photocell of the spectrophotometer. A 1.0% w/v solution of the polymer in C_6H_6 was progressively titrated with methanol containing 0.1% of the antioxidant. The absorbance was recorded directly from the galvanometer after each successive addition of methanol and a turbidimetric titration curve for each polymer sample was drawn, as shown in *Figure 2*, after making concentration corrections to the absorbance readings.

Coupling experiments

Preparation of living polystyrene. The living polystyrene samples were prepared in calibrated flasks, sealed under high vacuum, in a way similar to the procedure described elsewhere[22]. In separate experiments, four different solvent media and two different initiators were employed under experimental conditions outlined below:

(i) PS^-Li^+, prepared in pure benzene, initiated by n-BuLi, at a temperature of 20°C, for 24 h.

(ii) PS^-Li^+, prepared in pure toluene, initiated by n-BuLi, at a temperature of 20°C, for 24 h.

(iii) PS^-K^+, prepared in pure THF, initiated by cumyl-K, polymerized first at −78°C for 15 min and then at 0°C for 4 h.

(iv) PS^-Li^+, prepared in benzene containing a small amount of added THF (C_6H_6:THF = 12:1 v/v in the final reaction mixture), initiated by n-BuLi, at 20°C for 8 h.

In all polymerization reactions, the main solvent was distilled directly into the polymerization flask. The initiator, monomer and the added polar solvent (THF) were then successively added from separate ampoules joined to the flasks through breakseals. In all cases, monomer was added dropwise over a period of 15 min. Particular care was taken to maintain a uniform reaction temperature during the initial stages of polymerization. Efficient stirring was maintained throughout the reaction.

Preparation of PECH solutions for coupling reactions. A known weight of the previously purified PECH dissolved in distilled benzene was filtered into the coupling reaction flask and freeze-dried for 48 h. The freeze-dried polymer was then dissolved in a suitable solvent such as benzene, toluene, or THF, and kept under argon before coupling.

Coupling reactions. The living polymer solution was syringed out of the polystyrene flask under a positive pressure of argon introduced into the flask through a break-seal. This polymer solution was then added dropwise over a period of 15–20 min through a rubber septum into the PECH solution stirred vigorously with a magnetic stirrer.

A portion of the living polystyrene sample, used in each coupling experiment, was separately terminated by addition of a trace of degassed methanol and finally isolated by precipitation into excess methanol. The molecular weight of this terminated PS, as determined by g.p.c., was assumed to be equal to the molecular weight of the PS grafts, $\bar{M}_n$ (PS), in the graft copolymer.

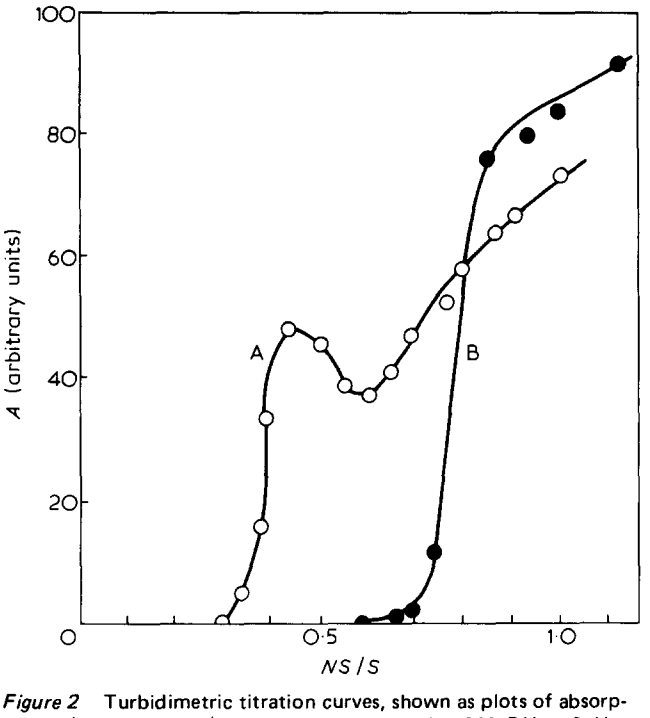


Figure 2 Turbidimetric titration curves, shown as plots of absorption *A* (arbitrary units) against the volume ratio of MeOH to C_6H_6, *NS/S*. (A), Polymer G7, from experiment 7, consisting of P(ECH-*g*-S), and PS (○); (B), PS sample isolated by separate termination of the living PS^- used in experiment 7 (●); initial polymer concentrations = 1% w/v in C_6H_6

Table 1 Coupling reaction conditions and polymeric reaction product designation

Expt. No.	Solvent for PS^-Li^+	Solvent for PS^- Ki^+	10^2 x Conc. of PS^- (mol dm^{-3})	Solvent for PECH	Conc. of PECH (g dm^{-3})	10^2 x R†	%PS w/w in coupling reaction mixture	Coupling reaction temp. (°C)	Final appearance of reaction mixture	Total polymer product designation††	Separated purified graft copolymer designation
1	C_6H_6	–	1.67	C_6H_6	10.00	12.99	90.2	20	Colloidal	G1	G1–G
2	C_6H_5–CH_3	–	2.66	C_6H_5–CH_3	10.00	16.84	91.3	−78	Colloidal	G2	G2–G
3	C_6H_6*	–	1.83	C_6H_6	6.25	13.77	89.0	20	Hazy	G3	G3–G
4	–	THF	1.23	THF	10.00	8.56	92.5	20	Clear	G4	G4–G
5	C_6H_6*	–	1.83	THF**	25.00	3.39	66.6	20	Clear	G5	G5–G
6	C_6H_6*	–	1.83	THF**	12.50	7.00	80.5	20	Clear	G6	G6–G
7	C_6H_6*	–	1.83	THF**	5.00	18.45	91.6	20	Clear	G7	G7–G
8	C_6H_6*	–	1.83	THF**	2.00	42.37	96.1	20	Clear	G8	G8–G

* Benzene contained a small amount of THF (C_6H_6: THF = 12:1 v/v approx.)

** Final (THF/C_6H_6) ratio, v/v in the coupling reaction mixture, was 67/33 approx

† $R = \frac{\text{number of mol of added } PS^-}{\text{initial number of moles of Cl in PECH}}$ used in a coupling experiment

†† As isolated by precipitation into excess MeOH. Fractions G1A and G2A were soluble in MeOH and isolated separately from experiments 1 and 2, respectively

The coupling reaction conditions are summarized in *Table 1*. In all experiments, as each drop of the living polymer solution was added to the PECH solution, the characteristic red colour of the polymer disappeared almost instantaneously. The mixtures under all conditions were reacted for a period of about 1 h. The final reactant product mixtures showed visual differences as indicated in *Table 1*.

Isolation of total polymer and purification of the graft copolymers

The total polymer from each coupling experiment was precipitated into a five-fold excess of methanol in a Waring blender, redissolved in benzene to give an approximately 2% w/v solution, filtered through a porosity-3 glass sinter, reprecipitated into methanol containing 0.1 w/v antioxidant, and then dried at 45°C to a constant weight in a vacuum oven. Two polymer fractions, G1A and G2A, from the experiments 1 and 2, respectively, (*Table 1*), were soluble in the final solvent-excess methanol mixture. So a portion of the filtered solution was evaporated to dryness in a rotary evaporator to recover the brown-coloured sticky polymer fractions (about 2% w/w total polymer). No such polymer fractions were recovered from the other experiments.

The polymers G1–G8, isolated from the coupling experiments, consisted of a mixture of the graft copolymers, P(ECH-*g*-S) and homopolystyrene, PS. This was shown by the existence of two g.p.c. peaks, slightly overlapping in some cases, and also by separate turbidimetric titrations as illustrated in *Figure 2*, in which the corrected absorbance, *A*, in arbitrary units, is plotted against the volume ratio of non-solvent to solvent, NS/S, for initial 1% w/v solutions of the polymers.

Attempted isolation of the graft copolymers by extraction procedures using cyclohexane, carbon tetrachloride, and diethyl ether, were unsuccessful due to incomplete separation. Thus, cyclohexane, carbon tetrachloride, and diethyl ether, are non-solvents for PECH but solvents for polystyrene of $\bar{M}_n \sim 5 \times 10^3$ and were found to dissolve some of the graft copolymers. However, complete and quantitative separation of the graft copolymers from the reaction mixtures was usually satisfactorily performed by fractional precipitation, based on the results of the turbidimetric titrations and with sufficiently widely separated peaks, following the procedure described in the literature[23]. Successful separations of the graft copolymers were confirmed by the single g.p.c. peaks in the fractions G1-G – G8-G listed in *Table 1*.

The composition, structure and molecular weights of the graft copolymers

The grafting efficiency of PS^- in the coupling reactions was calculated from the relation:

$$\% \text{ grafting efficiency} = \left[\frac{\begin{array}{c}(\text{weight \% of PS/weight \% of PECH}) \\ \text{in a graft copolymer}\end{array}}{\begin{array}{c}(\text{weight \% of PS/weight \% of PECH}) \\ \text{used in a coupling experiment}\end{array}}\right] \times 100$$

The expected number average molecular weight, $\bar{M}_n$ (cal) of the graft copolymer was calculated from the relation:

$$\bar{M}_n(\text{cal}) = \bar{M}_n(\text{PECH}) + \frac{y'}{x'}\bar{M}_n(\text{PECH})$$

where x' and y' are the weight % of PECH and PS in the graft copolymer, and $\bar{M}_n$ (PECH) is the observed number average molecular weight of the starting PECH.

The degradation or cleavage factor, f, signifying the extent of backbone cleavage involved in the formation of a graft copolymer, was calculated from the relation $f = \bar{M}_n(\text{cal})/\bar{M}_n(\text{obs})$, where $\bar{M}_n$(cal) and $\bar{M}_n$(obs) are the calculated and observed number average molecular weights of a graft copolymer respectively.

The inverse graft frequency, λ is the number of substituted and unsubstituted ether units per PS-graft in a copolymer and was calculated from the % chlorine content in a graft copolymer and the known $\bar{M}_n$ value of the PS grafts.

Thus the %Cl for a graft copolymer gives the corresponding value of (*m/g*) and λ is expressed by the equation:

Table 2 Molecular weights, composition and structure of the P(ECH-*g*-S) copolymer samples

Polymer sample	% PS w/w		% Grafting efficiency	$10^2 \times R$	Molecular weights									
					Initial PECH	PS branch	Graft copolymers							
							Purified Sample			Sample in the mixture				
	U.v. analysis	micro-analysis			$\bar{M}_n \times 10^{-5}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_n$ (cal) $\times 10^{-5}$	$\bar{M}_n$ (obs) $\times 10^{-5}$	$\bar{M}_w$ (obs) $\times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$ (obs) $\times 10^{-5}$	$\bar{M}_w$ (obs) $\times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	f	λ
G1–G	–	84.5	59.2*	12.99	1.61	6.59	10.39	0.53	1.47	2.77	0.49	0.80	1.65	21.20	14.2
G2–G	–	87.1	64.3*	16.84	1.61	5.75	12.48	0.41	1.20	2.91	0.52	0.81	1.57	24.0	10.3
G3–G	86.6	85.5	79.9**	13.77	3.49	5.45	26.04	1.69	4.32	2.55	1.50	2.78	1.85	17.36	11.1
G4–G	–	86.8	53.3*	8.56	0.44	13.37	3.33	–	–	–	3.62	10.72	2.96	–	23.0
G5–G	46.7	47.1	43.3**	3.39	3.49	5.45	6.55	–	–	–	6.19	21.04	3.40	1.06	67.8
G6–G	65.3	65.1	45.6**	7.00	3.49	5.45	10.06	8.11	33.24	4.10	7.69	22.99	2.99	1.31	32.9
G7–G	85.7	84.7	55.0**	18.45	3.49	5.45	24.40	7.70	37.02	4.80	7.90	27.43	3.47	3.09	11.8
G8–G	98.1	95.1	76.7*	42.37	3.49	5.45	71.22	5.20	16.61	3.19	4.97	12.47	2.51	14.33	4.1

* Grafting efficiency of PS^- was calculated from the PS content of the graft copolymers obtained by microanalysis
** Grafting efficiency was calculated from the PS content obtained by u.v. analysis

$$\lambda = \frac{m+g}{g} = (m/g)+1$$

In these calculations, the elemental composition of the original PECH was assumed to be the same as that of its repeat unit.

The molecular weight of PS^-, and the molar ratio R. The molecular weight of PS^- used in a coupling experiment was assumed to be the same as the molecular weight of the living polymer separately terminated.

The ratio R, involved in a coupling experiment was defined:

$$R = \frac{\text{number of mol of added } PS^-}{\text{number of mol of Cl in PECH}}$$

The number of mol of added PS^- was calculated from the $\bar{M}_n$ of the separately terminated living PS^- used in a coupling experiment and the weight of PS used. The weight of PS used was calculated from the total amount of polymer isolated from a coupling experiment, and the initial amount of PECH used.

RESULTS AND DISCUSSION

P(ECH-*g*-S) copolymers have been synthesized by the carbanionic coupling or deactivation of living polystyrene at the pendant $-CH_2Cl$ groups of polyepichlorohydrin. The synthesis has been confirmed by characterization of the graft copolymers by i.r., u.v., g.p.c., elemental microanalysis and solubility characteristics. Some of the detailed results are presented in *Table 2*. The solubility characteristics of PECH were changed by grafting with polystyrene. A graft copolymer containing, for example, about 47% w/w PS (sample G5-G, *Table 2*), showed a solubility in benzene, toluene and THF intermediate between the values for the corresponding pure homopolymers, as expected. The grafting reactions were complicated by various side reactions. The nature of the side reactions was investigated by a study of the i.r. spectra of some degraded graft copolymers, comparison of the degradation factors of graft copolymers, *f*, prepared in different solvent media and a comparison of the g.p.c. results for the graft copolymers with those of the initial PECH samples. A separate study of the BuLi cleavage of PECH in solution was also made, and these results will be presented in a later paper.

The grafting reactions in pure hydrocarbon solvents such as benzene and toluene were accompanied by two distinct side reactions, (i) cross-linking and subsequent colloidal phase separation and (ii) degradation, including backbone cleavage. The cross-linking reaction was initially suggested by the formation of colloidal curd-like suspensions in the coupling experiments 1 and 2 (*Table 1*). Further evidence was that the graft copolymer samples G2 and G2-G showed a high molecular weight peak in their respective *MWD* curves (*Figure 3* (C) and (D)), peak III). The molecular weight of the polymer corresponding to peak III remained lower than that of the initial PECH, presumably due to simultaneous degradation. G1 and G1-G showed a similar behaviour. The polymer responsible for this high molecular weight tail was separated in experiment 2 and constituted about 2% w/w of the total graft copolymer. Subsequent microanalysis showed a negligible PS content in this fraction. However, the

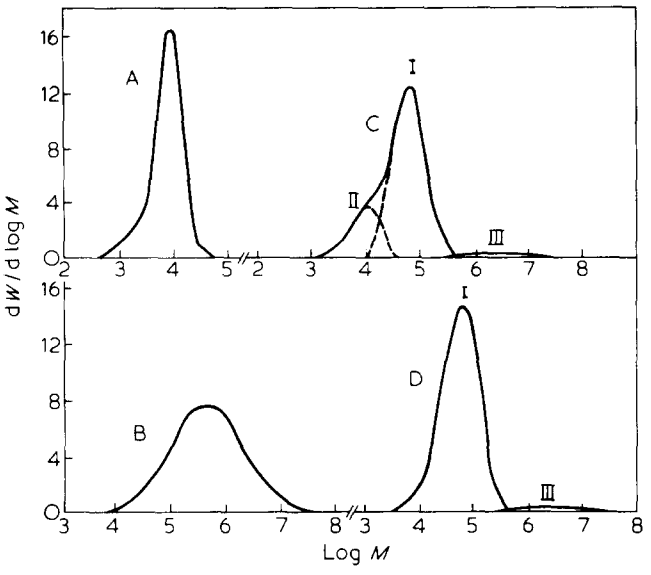


Figure 3 Differential molecular weight distribution curves. (A), Polystyrene sample from the separately terminated living PS^- used in the coupling experiment 2; (B), initial PECH sample used in the coupling experiment 2; (C), coupling reaction product G2; (D), graft copolymer sample G2–G

average PS content of the whole of the graft copolymer G2-G (*Table 2*), including the high molecular weight tail, was relatively high, being 87.1% w/w in comparison to 91.3% w/w used in this coupling experiment. But the $\bar{M}_n$ of the isolated total graft copolymer including the high molecular weight polymer was still lower than that of the starting PECH sample itself. This lowering in molecular weight of the PECH on grafting was due to backbone cleavage. The degradation of the backbone was also clear from the i.r. spectra of the methanol soluble degraded graft copolymer sample GIA (*Figure 1* (D)). This sample showed some additional absorption peaks, apart from the usual peaks for PECH and PS characteristic of a P(ECH-*g*-S) copolymer (*Figure 1*, A–C). The extra peaks were at wave numbers 3460 cm^{-1} (broad) due to –OH (hydrogen bonded), at 3295 cm^{-1} and 2120 cm^{-1} due to $-C\equiv CH$, at 1725 cm^{-1} due to C=O, at 1665 cm^{-1} due to α, β-unsaturated aldehyde or ketone, at 1630 cm^{-1} due to C=C conjugated to etheral oxygen, as in a vinyl ether, or a carbonyl group, as in an α, β-unsaturated aldehyde or ketone. The formation of these groups by the degradative reactions of PS^-Li^+ on PECH will be discussed later. Another feature of the coupling reactions in purely hydrocarbon solvents was that the *MWD* peak associated with homopolystyrene indicated an increase in molecular weight after any grafting experiment (Peak II, *Figure 3* (C)). This may be due in part to coupling between PS^-Li^+ and PS-Cl species arising from lithium–halogen interchange. The results of experiment 2 in toluene at −78°C showed that the side reactions such as cross-linking and degradation occurred even at this low temperature. When the coupling reaction was carried out in C_6H_6 in the presence of a small amount of polar solvent such as THF, (experiment 3), the cross-linking reaction was eliminated to a great extent.

In the coupling experiment 4, carried out in THF using PS^-K^+, no cross-linking was observed and degradation was also not marked. In the series of coupling experiments 5–8, using PS^-Li^+, cross-linking was apparently completely avoided and degradation minimized in the mixed solvents THF–C_6H_6. Thus the $\bar{M}_n$ values of all the graft copolymers in the series were higher than those of the initial PECH backbone polymers (*Figure 6*). The cleavage factor *f*, plotted against *R* (*Figure 7*) indicated that the extent of backbone cleavage increased with increase in the amount of living polymer used. For a ratio of *R* less than 0.1, the amount of degradation was negligibly small.

The average inverse graft frequency in the most degraded graft copolymer, sample G8-G, as calculated from the % Cl, was 4.1, which means that there was one polystyrene graft for every four ether repeat units in the PECH backbone. The high average inverse graft frequencies in this and other graft copolymers of the series G5-G–G8-G (*Table 2*) indicated that PECH can be grafted without severe degradation in a polar solvent, such as THF, or in THF/C_6H_6 mixtures, using living PS^- with either lithium or potassium as counter ions.

The PS contents in the series of graft copolymers, G5-G–G8-G, prepared in THF/C_6H_6 showed an increase from 46.7% to 95.1% with an increase in the molar ratio, *R* used in their synthesis. The grafting efficiency of PS^- also increased from about 43% to about 77% when plotted against molar ratio *R* (*Figure 5*). The grafting efficiency is always less than 100% and the reasons for this may be two-fold: (i) termination of living polymer chains due to various degradative side reactions, and (ii) termination of some living polymer chains by impurities in the PECH-solvent mixtures. The increase in grafting efficiency with an increase in *R*, in spite of the greater amount of degradative termination of the living polymer, may be due to a proportionately decreasing % of impurity content in the total reaction systems at higher *R* values.

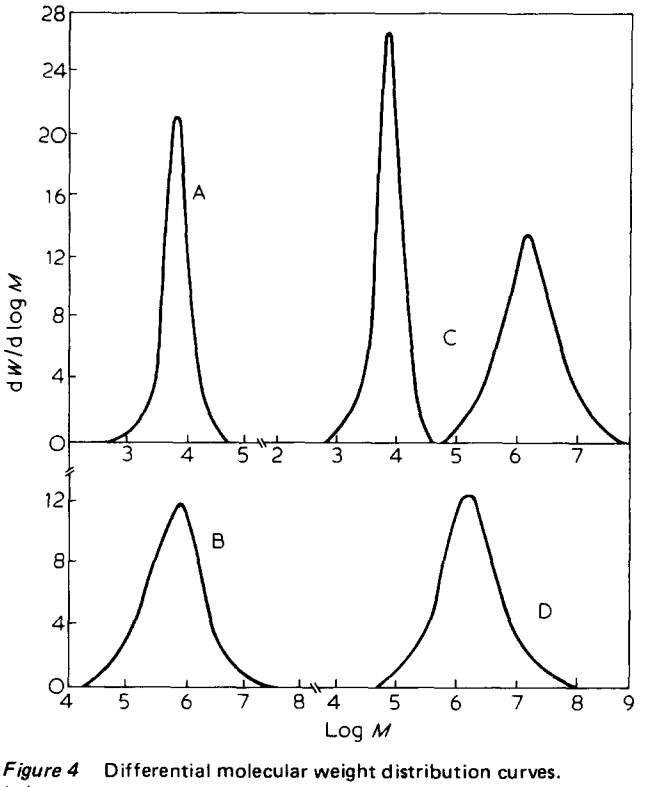


Figure 4 Differential molecular weight distribution curves. (A), Polystyrene sample from the separately terminated living PS^- used in the coupling experiment 7; (B), initial PECH sample used in the coupling experiment 7; (C), coupling rj action product G7; (D), graft copolymer sample G7–G

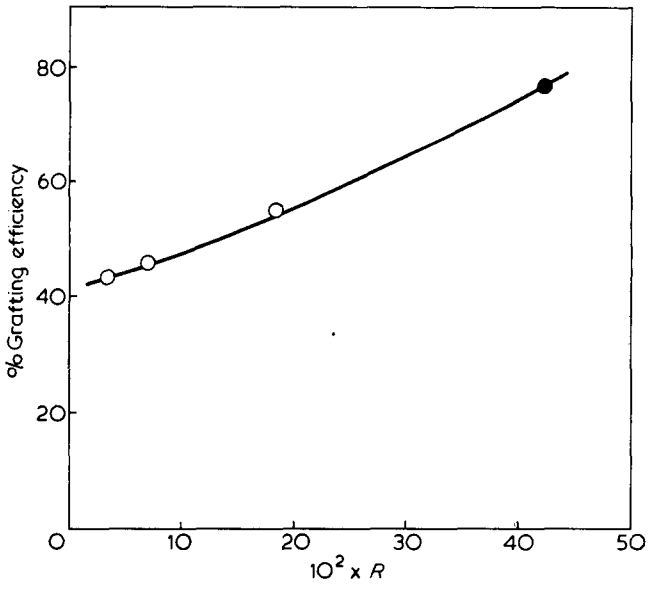


Figure 5 Grafting efficiency of PS^- as a function of R in the coupling experiments 5–8 carried out in THF–C_6H_6 mixtures: ○, calculated from u.v. analysis; ●, calculated from microanalysis

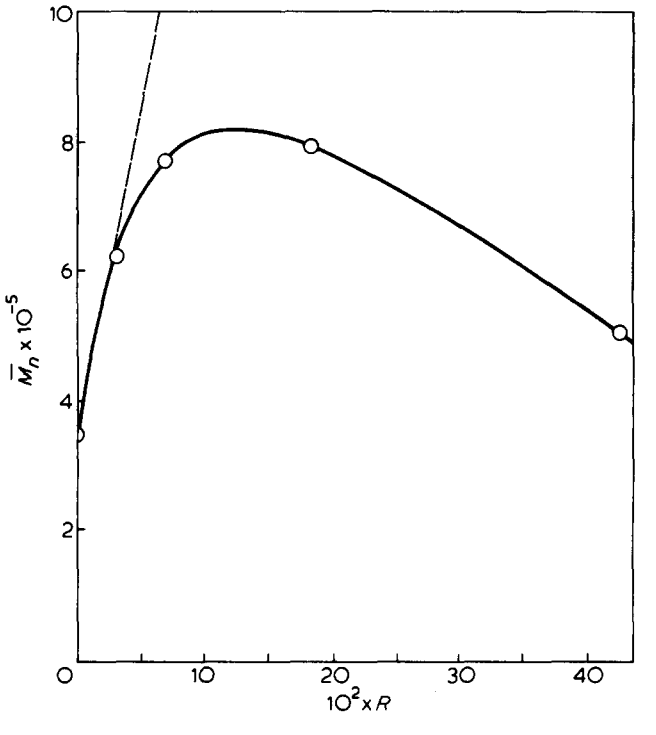
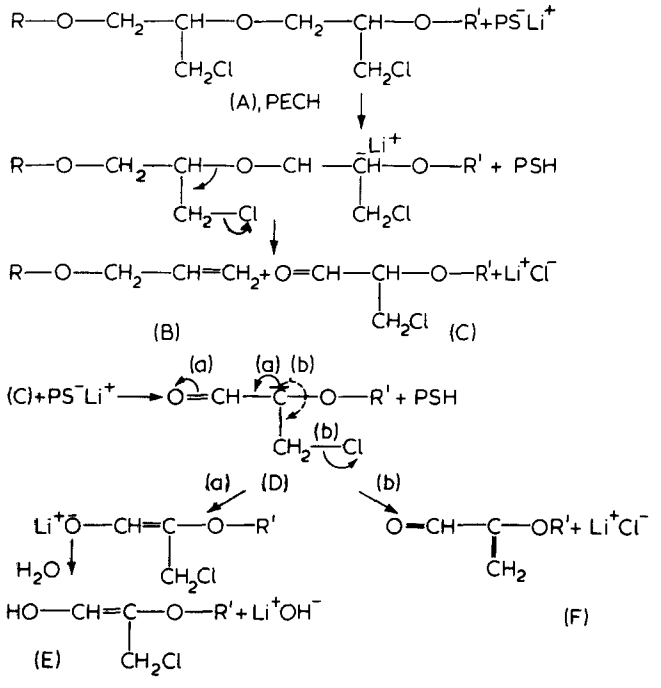


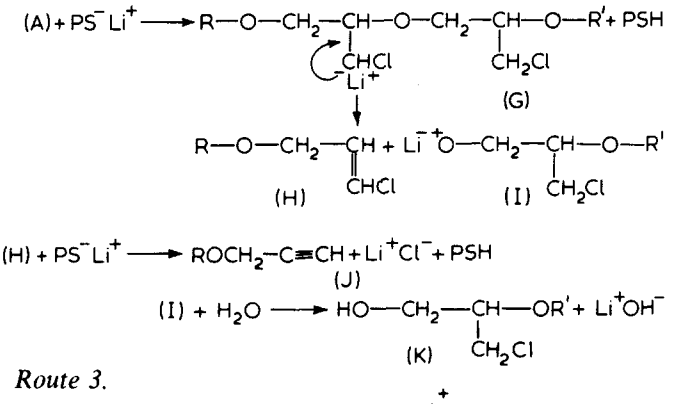
Figure 6 Number average molecular weights, $\bar{M}_n$, of the graft copolymer samples G5-G – G8-G vs. the molar ratio R used in their synthesis: ○, observed values; – – – –, line calculated assuming no degradation

Investigation of the *MWD* results (*Figures 3* and *4*), and the molecular weights of the graft copolymers prepared in different solvent media, suggested that the side reactions are relatively less important in polar solvent media such as THF and THF/C_6H_6 mixtures. This may indicate that a solvent ion-pair is more effective in carbanionic coupling reactions than a tight ion-pair. However, a tight ion-pair is associated with more degradative side reactions. Possible mechanisms leading to the formation –OH, –C≡CH, and simple and allylic carbonyl groups, are given below:

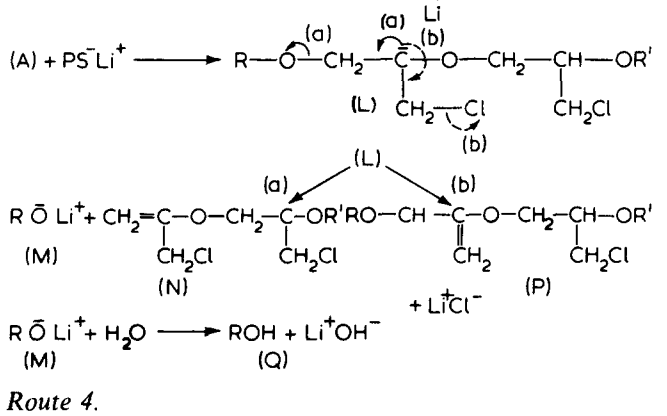
Route 1.



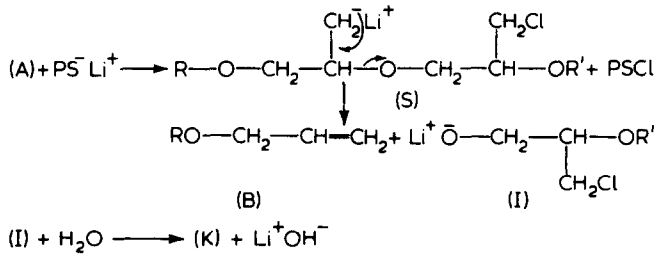
Route 2.



Route 3.



Route 4.



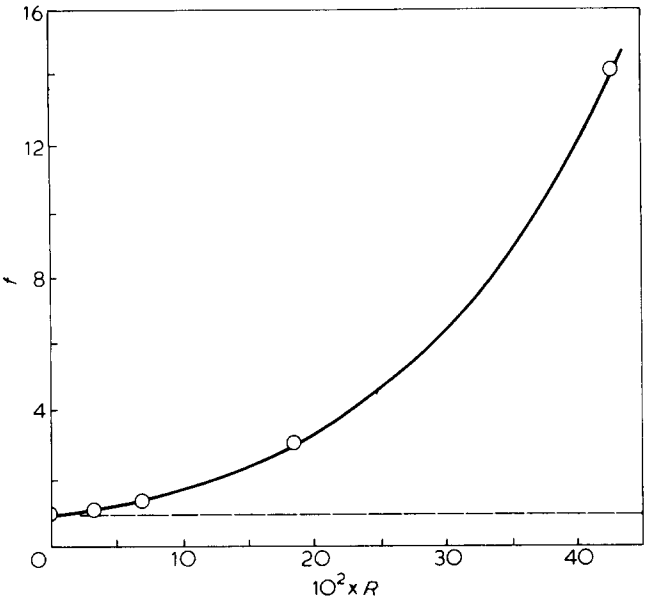


Figure 7 The cleavage factor, *f*, for the graft copolymer samples, G5-G–G8-G, prepared in THF–C_6H_6 mixtures, as a function of *R*. ○, observed values; – – – –, line calculated assuming no degradation

The product (S), formed by lithium–halogen interchange, may couple with the chloromethyl group of another PECH chain resulting in a cross-linked polymer.

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