Anionic synthesis of poly(epichlorohydrin-*g*-styrene) and chemical modification of polyepichlorohydrin

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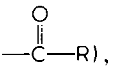
Poly(epichlorohydrin-*g*-styrene) copolymers, P(ECH-*g*-S)s, have been prepared in solution by two different methods of coupling polyepichlorohydrin, PECH, with polystyrene, PS, containing a functional end group. In the first method, polystyryl carboxylic acid, PSCOOH, prepared from living polystyrene, was converted to the corresponding potassium salt which was coupled with PECH in dimethyl formamide solution usually at 60°C. In the second method, polystyryl potassium, $PS^- K^+$, in tetrahydrofuran solution was end-capped with propylene sulphide to form $PSCH_2CH(CH_3)S^-K^+$ which was coupled directly with PECH in tetrahydrofuran at 40°C. Grafting by the first reaction was relatively slow but occurred without significant adverse side reactions. The grafting by the second reaction was relatively fast, but side reactions occurred resulting in a cleavage of the graft copolymer. The graft copolymers were purified by fractional precipitation and extraction procedures and were characterized by infra-red and ultra-violet spectroscopy, microanalysis, gel permeation chromatography, differential scanning calorimetry, solution viscometry, dynamic mechanical testing, and electron microscopy. Solution properties of the graft copolymers in benzene–carbon tetrachloride and toluene–cyclohexane mixtures were studied. There was evidence of micelle formation in dilute solutions of the mixed solvents and microphase separation of components in the solid state. Nucleophilic substitution of chlorine atoms in PECH by phenyl acetate ($C_6H_5CH_2COO-$) and thiophenoxide (C_6H_5S-) groups was performed.

Keywords Characterization; synthesis; poly(epichlorohydrin-*g*-styrene); copolymers; modification; polyepichlorohydrin; functional group

INTRODUCTION

It has been shown previously[1,2] that a good nucleophile with a relatively weak basic character is a suitable reagent for coupling with epichlorohydrin (ECH) polymers at the chloromethyl ($-CH_2Cl$) side chains. This combination of properties is sometimes difficult to achieve, however, since strongly nucleophilic reagents are usually also strongly basic.

P(ECH-*g*-S) copolymers have been prepared before[2,3] by anionic coupling reactions between PECH and living polystyryl anions, PS^-. During such coupling reactions, degradative cleavage of the PECH backbone polymer, induced by PS^- anions, has also been found to occur[2].

Modification of ECH polymers involving nucleophilic substitution of Cl by other groups, such as ether (–O–R)[4], thioether (–S–R)[5,6], and ester  $(-O-\overset{O}{\overset{\|}{C}}-R)$, has been achieved previously, without significant degradation of the PECH backbone. In such modifications, alkali metal salts of alcohols, phenols, thiols, thiophenols, and carboxylic acids, were used as the modifying nucleophiles. Polymeric molecules, having functional end groups similar to those mentioned above, have not been used before, however, to synthesize graft copolymers.

This paper describes the synthesis of P(ECH-*g*-S) by coupling polyepichlorohydrin with polystyrene containing a functional end group, prepared by two different methods. In the first method, each living polystyrene molecule was capped with a COOH end group and subsequently the potassium salt was used for coupling. In the second method, polystyryl potassium, PS^-K^+, was end-capped with propylene sulphide to form $PSCH_2CH(CH_3)S^-K^+$ which was then used for coupling.

The introduction of COOH end groups into polystyrene has been discussed elsewhere[8,9]. The introduction of propylene sulphide end groups, $-CH_2CH(CH_3)S^-$, was carried out in a similar way to the capping of polystyryl sodium with ethylene oxide[10]. The present paper also describes exploratory modification of PECH with the potassium salt of phenyl acetic $C_6H_5CH_2COOH$ and also with sodium thiophenoxide, $C_6H_5S^-Na^+$.

EXPERIMENTAL

Reagents and purification

Benzene, C_6H_6 (Koch-Light Lab. Ltd.), *Tetrahydrofuran*, THF (Hopkins and Williams), and *Styrene* (BDH) were purified and stored as described elsewhere[2].

n-*Butyl lithium*, *n*-BuLi (Alpha Products) and *Cumyl potassium*, cumyl-K (Orgmet Inc., Hamstead, N.H., U.S.A.), were diluted and analysed as described elsewhere[2].

Phenyl acetic acid, $C_6H_5CH_2COOH$ (Hopkin and Williams), 99% w/w pure and *Thiophenol*, C_6H_5SH (Aldrich Chemical Co.) were used without further purification.

Sodium thiophenoxide, $C_6H_5S^-Na^+$, used for the modification of PECH, was prepared from thiophenol

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and metallic sodium and purified according to the procedure described elsewhere[11]. The reagent was stored in a vacuum desiccator in a cool dark place until required.

Metallic sodium, as freshly cut pieces, after cleaning with petroleum ether, was used as required.

Propylene sulphide (Aldrich Chemical Co.) 98% w/w pure, was dried over powdered calcium hydride and distilled immediately before use. The middle fraction was used in further experiments.

N,N-*Dimethylformamide*, DMF (BDH), was dried over activated Linde 4A molecular sieve and then distilled under reduced pressure. The middle fraction was used.

Potassium hydroxide, KOH (Hopkin and Williams, AR grade), and *Methanol*, MeOH (BDH, AR grade) were used without further purification in the preparation of methanolic KOH solutions. *Succinic acid* (BDH, AR grade) was used in aqueous solution, for the standardization of methanolic KOH solutions.

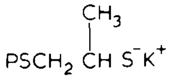
Polyepichlorohydrin, PECH, used as the backbone polymer, was obtained by rough fractional precipitation of 'Herchlor H' (Hercules Inc.) from 2% w/v benzene solution, using MeOH containing 0.1% w/v antioxidant, Topanol CA (ICI Ltd.), as precipitant. The middle fraction was retained, reprecipitated from benzene solution in a Waring blender using MeOH and dried to constant weight in a vacuum oven at 50°C. *MeOH* (BDH, Tech. grade), containing 0.1% w/v Topanol CA as antioxidant, was used directly in precipitations of all PECH and P(ECH-*g*-S) samples.

Synthesis

Preparation of living PS⁻ and end-capping:

(a) *End capping to give* $PSCOO^-K^+$: Polystyryl lithium, PS^-Li^+, initiated by *n*-BuLi was prepared in benzene containing a small amount of added THF (C_6H_6:THF = 8:1 v/v approx.) in a sealed flask, at room temperature, according to the procedure described elsewhere[12]. The living polymer was terminated by carbon dioxide, by forcing out the polymer solution from the reaction flask into a slurry of solid CO_2 in purified THF. This operation was performed under argon, by means of a length of steel tubing introduced through a breakseal into the reaction flask. The terminated polymer was precipitated in a ten-fold excess of MeOH containing 0.1% v/v HCl, redissolved in THF, reprecipitated in ice-cold methanol, washed successively with methanol and distilled water on a sintered glass funnel to remove any unreacted HCl, and finally dried to constant weight at 50°C in a vacuum oven. PSCOOH thus prepared was analysed by end group titration and the molecular weight estimated.

A weighed amount of PSCOOH of known number average molecular weight, $\bar{M}_n$, dissolved in DMF was titrated with 0.1 0.2 M KOH in MeOH solution up to the neutralization point, using phenolphthalein, to prepare the $PS\,COO^-K^+$ in DMF solution, later used for coupling with PECH.



(b) *End-capping to give* $PSCH_2\overset{CH_3}{\overset{|}{C}H}S^-K^+$ Polystyryl potassium, initiated by cumyl-K, was prepared in THF at −78°C, and at 0°C, according to the procedure described elsewhere[12]. It was terminated under an argon atmosphere, by dropwise addition of propylene sulphide, just up to the disappearance of the characteristic red colour of the living polymer. Since propylene sulphide may be polymerized anionically[13], addition of excess sulphide was avoided in these experiments.

A portion of the $PSCH_2CH(CH_3)S^-K^+$ thus formed, was precipitated in MeOH while the rest was used for coupling with polyepichlorohydrin.

Coupling reactions

(a) *Between PECH and* $PSCOO^-K^+$. A weighed amount of PECH containing ~0.2% w/w antioxidant was dissolved in DMF in a two-necked reaction flask, provided with a reflux condenser and a drying guard tube. The requisite amount of PSCOOH, neutralized to form $PSCOO^-K^+$, was added. The mixed solution was diluted with more DMF to give a 1% w/v of PECH and heated under a slow stream of oxygen-free nitrogen at 60°C or other selected reaction temperature for the desired period of time, with constant magnetic stirring. A liquid paraffin thermostat bath was used in these experiments.

After the reaction period, the solution was cooled immediately, filtered and the polymer precipitated in MeOH containing antioxidant, and dried as before.

Purification of the graft copolymers: The polymer isolated from a coupling experiment, was found to be a mixture of two polymers, a graft copolymer and homopolystyrene, as shown by the g.p.c. results. The graft copolymer was quantitatively separated from the mixture by a fractional precipitation procedure based on the g.p.c. results and turbidimetric titration results obtained by experiments described elsewhere[2]. An essentially quantitative separation of the graft copolymer from the homopolymer was achieved using a 1% w/v solution of the polymer mixture in C_6H_6 and using methanol containing 0.1% w/v antioxidant, as precipitant. The graft copolymers were twice purified by this technique, and the final samples showed single peaks in their respective g.p.c. traces. Two main series of graft copolymers, series-1 and series-2, using PSCOOH samples PS-1 and PS-2 (*Table 1*) were prepared.

For analysis of the graft copolymers by u.v. and microanalysis, the polymers were freed from antioxidant by reprecipitation and subsequent washing of the reprecipitated polymer with MeOH containing no antioxidant.

(b) *Between PECH and* $PSCH_2CH(CH_3)S^-K^+$. $PSCH_2CH(CH_3)S^-K^+$, at a concentration of 2.31×10^{-3} mol dm^{-3} in THF, was added under argon pressure to a 2% w/v solution of PECH in THF also under argon. In two separate experiments, 0.606×10^{-4} and 1.26×10^{-4} moles of end-capped polystyrene ($\bar{M}_n = 4.54 \times 10^4$), respectively, were added to 1 g of antioxidant-free PECH ($\bar{M}_n = 2.20 \times 10^5$) dissolved in THF. The mixed polymer solution was stirred under argon at 40°C for 1 h and the reaction was then slowed down by addition of MeOH and cooling to room temperature. The polymers were immediately precipitated from the THF MeOH solution by adding more MeOH containing antioxidant and were then isolated and dried *in vacuo*.

Purification of the graft copolymers: The polymer mixture from each of these coupling experiments, was found, unexpectedly, to give a single but broader g.p.c. peak. Thus the $\bar{M}_n$ of the mixed polymers was almost equal to that of separately terminated living polystyrene used to produce the grafts. The PECH and graft

Table 1 Molecular weights of polystyrene samples used for grafting reactions

Polymer sample	End group	Molecular weights Predicted $\bar{M}_n \times 10^{-3}$	Observed $\bar{M}_n \times 10^{-3}$ End-group titration method	Osmometry	G.p.c.	$\bar{M}_w/\bar{M}_n$ (g.p.c.)
PS–1	–COOH	2.49	3.31	3.12	2.41	1.39
PS–2	–COOH	4.84	7.49	5.95	4.51	1.38
PS–3	–COOH	30.50	–	–	36.90	3.08*
PS–4	$-CH_2CH(CH_3)S^-K^+$	41.20	–	–	45.40	1.79

* A wider molecular weight distribution due to uneven stirring

copolymer were therefore both thought to have undergone backbone cleavage resulting in a decrease in molecular weight. The graft copolymer was successfully separated from ungrafted homopolystyrene, by several extractions with cyclohexane at 40°C. Thus, cyclohexane at 40°C was found to be a solvent for polystyrene but a non-solvent for PECH and those P(ECH-*g*-S) copolymers with relatively low graft frequency. An attempt to purify the graft copolymers by extraction with coiling cyclohexane in a Soxhlet apparatus was unsuccessful since it resulted in the extraction of substantial amounts of both the graft copolymers and homopolystyrene.

Modifications of PECH by small ions:

(a) *using potassium phenyl acetate,* $C_6H_5CH_2COO^-K^+$. In a single experiment, phenyl acetic acid (1.08 g) dissolved in DMF (40 cm^3) was neutralized with 1 M KOH in MeOH using phenolphthalein as indicator, and then mixed with PECH (1.00 g) dissolved in DMF (40 cm^3) in a reaction flask. More DMF was added and the diluted mixed solution (1% w/v in PECH), was heated in a slow stream of nitrogen at 60°C for 10 h with constant magnetic stirring. The polymer was precipitated into MeOH, washed several times with fresh methanol to remove any unreached $C_6H_5CH_2COO^-K^+$ and finally dried *in vacuo*.

(b) *using sodium thiophenoxide.* $C_6H_5S^-Na^+$ (0.71 g) was added to PECH (1.00 g) dissolved in DMF (100 cm^3). The ratio (moles of $C_6H_5S^-Na^+$:moles of Cl in PECH), *W*, was 0.50. The mixture was heated under a slow stream of nitrogen at 60°C for 10 h. The resulting polymer, only slightly soluble in DMF and other common solvents for PECH, was twice precipitated from a dispersion in DMF by addition to an excess of MeOH, filtered, washed several times with fresh MeOH to remove any unreacted $C_6H_5S^-Na^+$ and finally dried *in vacuo*. In another similar experiment, the value of *W* was 1.51.

Characterization of polymers

(*i*) *End-group titration.* PSCOOH samples in DMF solution, (~0.5 g in 25 cm^3) were titrated against freshly prepared 2.5×10^{-2} M KOH in MeOH, using phenolphthalein as indicator. A blank titration using an equal volume of DMF was also carried out. The presence of any free amine in DMF is undesirable and its absence was confirmed, using 1-fluoro-2,4-dinitrobenzene[14], before titration experiments. The molecular weights calculated from the amounts of KOH needed in three separate titrations agreed within 3% for each PSCOOH sample.

(ii) *Vapour pressure osmometry.* Number average molecular weights of PSCOOH samples were measured by vapour pressure osmometry using a Knauer Vapour Pressure Osmometer. Measurements were made at 37°C, using toluene as solvent and the instrument was calibrated with benzil.

(iii) *Gel permeation chromatography* (*g.p.c*). G.p.c. measurements of the PECH, P(ECH-*g*-S), modified PECH and PS samples, 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.

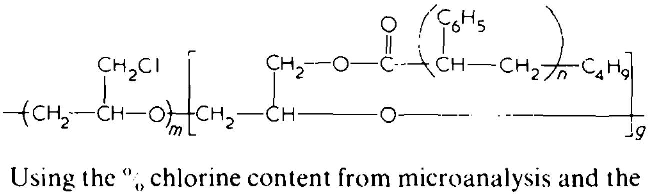
(iv) *Infra-red* (*i.r.*). I.r. spectra of the modified PECH and P(ECH-*g*-S) samples, were recorded with a Perkin Elmer 157G Grating Spectrophotometer, using thin films of the polymers directly cast onto NaCl plates from chloroform solutions. The spectral peaks of the graft copolymer samples consisted of those due to PECH and ungrafted PS. The ratio of the peak heights characteristic of polyether and polystyrene in the graft copolymers varied with the copolymer composition, as expected.

(v) *U.v. spectroscopy and graft copolymer composition:* U.v. measurements with the PECH, P(ECH-*g*-S) and PS samples, free from antioxidant, were made in chloroform solution, using a Perkin-Elmer 137 UV Spectrophotometer, according to the procedure described elsewhere[2,15]. The weight fraction of polystyrene in a graft copolymer, *y*, was calculated using the equation:

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

where E^*_{graft}, E^*_{PS} and E^*_{PECH} are the specific extinction coefficients for the P(ECH-*g*-S), polystyrene and PECH, respectively. It was found previously[2] that the E^*_{PS} and E^*_{PECH} were constant values independent of the chain lengths of the respective homopolymers. It was assumed that the small number of ester or thioether linkages in the grafted chains made a negligible contribution to the specific extinction coefficients characteristic of PS or PECH.

(vi) *Microanalysis:* Elemental microanalysis of PECH, modified PECH and P(ECH-*g*-S) samples were carried out for carbon, hydrogen and chlorine content, and also for the sulphur content of the thiophenoxide-modified PECH. The general formula of a graft copolymer formed through ester linkages, may be represented as:



Using the % chlorine content from microanalysis and the number average molecular weight of PS grafts, $\bar{M}_n$(PS).

measured separately, *m/g* values and % PECH and % PS contents in any copolymer were calculated by methods described elsewhere[2]. These % PS and % PECH contents in any graft copolymer agreed within 0.5% with the values obtained independently by u.v. analysis.

(vii) *Viscometry:* Limiting viscosity numbers, $[\eta]$, of the PECH and P(ECH-*g*-S) samples were measured in toluene at 30°C using a modified Ubbelohde suspended level viscometer. The limiting viscosity numbers of series 1 graft copolymers, formed through ester linkages, using the same initial PECH backbone polymer and the same polystyrene branch polymer, were measured as a function of Y/X, where Y/X is the ratio, (wt % PS/wt % PECH), in a graft copolymer.

Limiting viscosity numbers of some graft copolymers and also of the PECH samples used in their synthesis, were measured in benzene–carbon tetrachloride mixtures, as a function of solvent composition, at 25°C. Similar measurements were also made in toluene–cyclohexane solvent mixtures at 40°C. Benzene and toluene are good solvents for both PECH and PS, whereas carbon tetrachloride and cyclohexane (40°C) are good solvents for PS but non-solvents for PECH.

(viii) *Differential scanning calorimetry:* Thermal analyses of the P(ECH-*g*-S)s, formed through ester linkages, and the component PECH and PS samples were carried out, using a DuPont-900 Thermal analyser, fitted with a Differential Scanning Calorimetry cell.

The PECH and P(ECH-*g*-S) samples dissolved in C_6H_6 were placed in the d.s.c. pans and the solvent was allowed to evaporate, before the polymers were dried in a vacuum oven at 60°C for 72 h. PS samples were, however, used directly as fine dry powders. Graft copolymer samples, previously dried in the d.s.c. pans and thermally analysed were subsequently heated at 105°C for 24 h in a vacuum oven and again thermally analysed. In the discussion, the latter samples will be described as preheated samples.

(ix) *Mechanical properties:* The dynamic mechanical testing of some graft copolymer samples was performed, using a direct-reading dynamic viscoelastometer, the Rheovibron (Model DDV-II-C, Toyo Baldwin Co. Ltd.). Small strips of the polymer film, about 0.5 mm thick, were prepared by the slow evaporation of the solvent from the samples in benzene solution cast onto a mercury surface. Tan δ measurements were made with a heating rate of 2°C min^{-1}.

(x) *Transmission electron microscopy:* Morphological investigation of a graft copolymer sample was carried out with a JEM 100B transmission electron microscope (JEOL Ltd.), using thin sections (900–1000 Å thick), cut from the tough elastomeric polymer sample, previously precipitated by MeOH from C_6H_6 solution and dried in the vacuum oven at 50°C. A JEOL JEM 100CX TEM Scan electron microscope was used for scanning the chlorine content.

Composition, structure and predicted molecular weights of graft copolymers

The % grafting efficiency of polystyrene anions in a coupling reaction was calculated from the relation:

$$\%\ \text{grafting efficiency} = \frac{(\text{wt.\% of PS/wt.\% of PECH}) \text{ in a graft copolymer}}{(\text{wt.\% of PS/wt.\% of PECH}) \text{ used in a coupling experiment}} \times 100$$

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

$$\bar{M}_n(\text{cal} = \bar{M}_n(\text{PECH}) + Y/X\ \bar{M}_n(\text{PECH})$$

where X and Y are the wt. % of PECH and PS in the graft copolymer, respectively, and $\bar{M}_n$(PECH) is the observed number average molecular weight of the initial PECH backbone polymer. The observed and predicted number average molecular weights, $\bar{M}_n$(obs) and $\bar{M}_n$(cal), respectively, were used to analyse results.

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:

$$f = \frac{\bar{M}_n(\text{cal})}{\bar{M}_n(\text{obs})}$$

The inverse graft frequency, (λ), is the number of substituted and unsubstituted ether units per PS-graft in a graft copolymer and was calculated using equations developed elsewhere[2].

The molar ratio R *and its reciprocal* R′ in a coupling experiment were defined:

$$R = \left(\frac{\text{number of moles of added PS anions}}{\text{number of moles of Cl in PECH used}}\right)$$

and $R' = \dfrac{1}{R}$.

Modified PECH

In modification experiments, the extent of substitution and substitution efficiency may be defined:

A = extent of substitution =

$$\left(\frac{\text{moles of Cl substituted}}{\text{moles of Cl in original PECH}}\right) \times 100$$

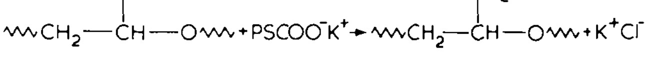
B = Substitution efficiency =

$$\left(\frac{\text{moles of Cl actually substituted}}{\text{maximum number of moles of Cl replaceable by the amount of reagent used}}\right) \times 100$$

RESULTS AND DISCUSSION

(a) *Graft copolymers formed by using* PSCOO$^-$K$^+$

(i) *Grafting reaction and efficiency:* Grafting of PSCOO$^-$ onto PECH, as expected, took place through the formation of ester linkages according to the reaction:



$$\sim\!CH_2\!-\!\underset{}{\overset{\overset{\displaystyle CH_2Cl}{|}}{C}H}\!-\!O\!\sim + PSCOO^-K^+ \rightarrow \sim\!CH_2\!-\!\overset{\overset{\displaystyle CH_2OOCSP}{|}}{C}H\!-\!O\!\sim + K^+Cl^-$$

Two series of graft copolymers, series-1 and series-2, using PSCOOH samples PS-1 and PS-2 of $\bar{M}_n$ (g.p.c.) equal to 2.41×10^3 and 4.51×10^3, respectively, were prepared by this reaction.

The graft copolymers were shown by separate experiments to be unstable towards KOH in

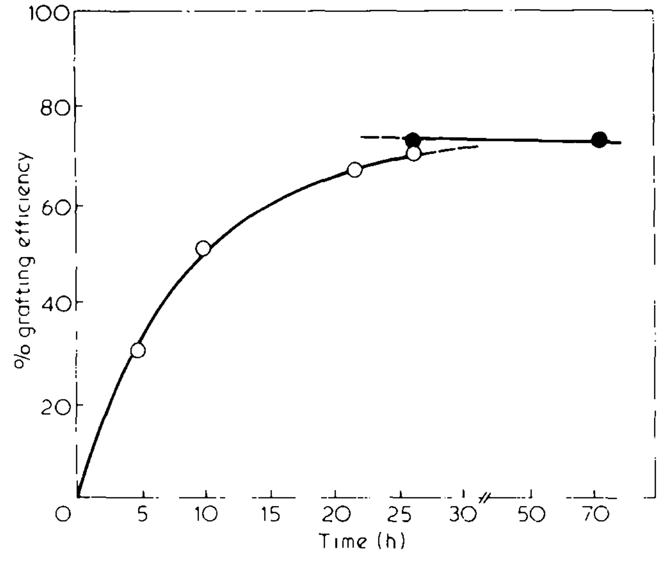
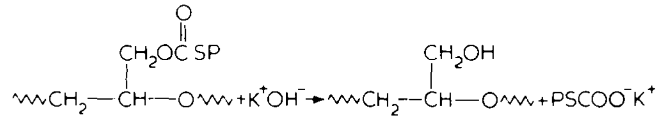


Figure 1 Grafting efficiency of $PSCOO^-$ onto PECH at 60°C as a function of time. PSCOOH sample PS–2 used. ○, *R'* = 16.4; ●, *R'* = 48.7

DMF/MeOH homogeneous solution at room temperature, due to hydrolysis of ester groups.



$$\sim\!\sim CH_2-\overset{\overset{\displaystyle CH_2OC(=O)SP}{|}}{CH}-O\sim\!\sim + K^+OH^- \rightarrow \sim\!\sim CH_2-\overset{\overset{\displaystyle CH_2OH}{|}}{CH}-O\sim\!\sim + PSCOO^-K^+$$

The regeneration of $PSCOO^-K^+$ can lead, under suitable conditions, to further nucleophilic attack on unsubstituted CH_2Cl groups in the graft copolymer.

At higher temperatures, alkalies are known to lead to degradative attack on a PECH backbone with a decrease in molecular weight[16]. Thus in some of the series-2 experiments involving a slight excess of K^+OH^-, over that needed to neutralize the PSCOOH, the grafting efficiency of $PSCOO^-$ remained unchanged but an overall lowering of graft copolymer molecular weight occurred.

A comparison of the % grafting efficiencies of $PSCOO^-$ (sample PS-1) was made in two coupling reactions at 30°C and 60°C, respectively, using the same concentration of reagents and same molar ratio *R'* of 26.0 and the same reaction time of 26 h. The % grafting efficiency at 60°C was 85.2 whereas that at 30°C was only 26.7.

The % grafting efficiency of $PSCOO^-$ (sample PS-2), at 60°C was measured as a function of time, using the same molar ratio *R'* and the same concentration of reagents. The results are shown in *Figure 1*. The % grafting efficiency increased with time, reaching a limiting value, presumably corresponding to complete reaction, in a time dependent on the ratio *R'*, as shown in *Figure 1*. Thus with *R'* equal to 16.4, the limiting % grafting efficiency had not been attained after 26 h, whereas with *R'* equal to 48.7, the limiting % grafting efficiency had been reached before 26 h.

In the two series of graft copolymers, using PSCOOH samples PS-1 ($\bar{M}_n$ (g.p.c.) $= 2.41 \times 10^3$) and PS-2($\bar{M}_n$ (g.p.c.) $= 4.51 \times 10^3$), the grafting efficiency vs. *R* curves exhibit a common trend, as shown in *Figure 2*. Thus the grafting efficiency decreased as the value of *R* increased. This possibly indicated incomplete reaction at higher values of *R* (lower *R'*). However, at relatively low values of *R*, the reaction seemed to be complete and maximum grafting efficiency was attained. The highest grafting efficiency achieved with sample PS-2 was about 10% less than that of PS-1. The lower grafting efficiency of PS-2 may be partly due to the greater steric hindrance arising from the slightly longer branches of polystyrene already grafted, and partly due to any difference in the inactive polystyrene contents of PS-1 and PS-2. The inactive polystyrene molecules, without COOH end groups, could have been produced at various steps of the synthesis by termination of living polymer with adventitious impurities, especially moisture.

The molecular weights of those graft copolymers, prepared using precisely neutralized PSCOOH, were higher than those of the initial PECH samples. A comparison of the calculated (predicted) and observed $\bar{M}_n$ values for the series-1 graft copolymers as a function of (Y/X) is shown in *Figure 3*. The results suggest that $PSCOO^-K^+$ has only a relatively slight degradative effect on PECH, which is much lower than that of living ions, such as PS^-Li^+. Since backbone degradation of these graft copolymers was minimal, the increase with % grafting of the limiting viscosity number measured in toluene, as shown in *Figure 4*, was to be expected. Similar behaviour for these graft copolymers was also observed in other good solvents for PECH, including C_6H_6 and dioxane.

(ii) *Solution and bulk properties:* The limiting viscosity numbers in mixed solvents as a function of composition are presented in *Figures 5* and *6*. As the % of non-solvent for the backbone was increased in the solvent mixture, all of the P(ECH-*g*-S)s except that shown in *Figure 5* (sample 1) and PECH homopolymer showed a decrease in their limiting viscosity numbers, indicating a size shrinkage of these molecules. This size decrease was relatively greater for the PECH samples than P(ECH-*g*-S)s in both C_6H_6/carbon tetrachloride and toluene/cyclohexane solvent mixtures. At a certain composition, the PECH, unlike the P(ECH-*g*-S)s underwent precipitation, as indicated in *Figures 5* and *6*. The graft copolymer containing the relatively longer PS grafts gave a slightly colloidal

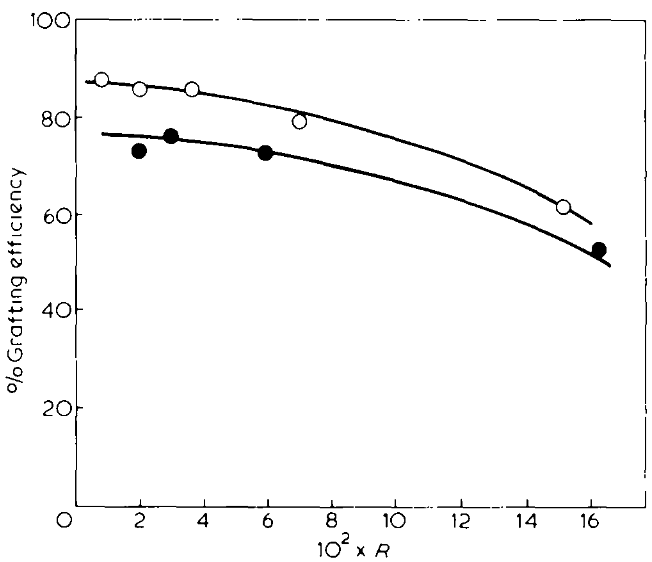


Figure 2 Grafting efficiency of $PSCOO^-$ onto PECH as a function of *R* at 60°C for a reaction time of 26 h. ○, PSCOOH sample used, PS–1; ●, PSCOOH sample used PS–2

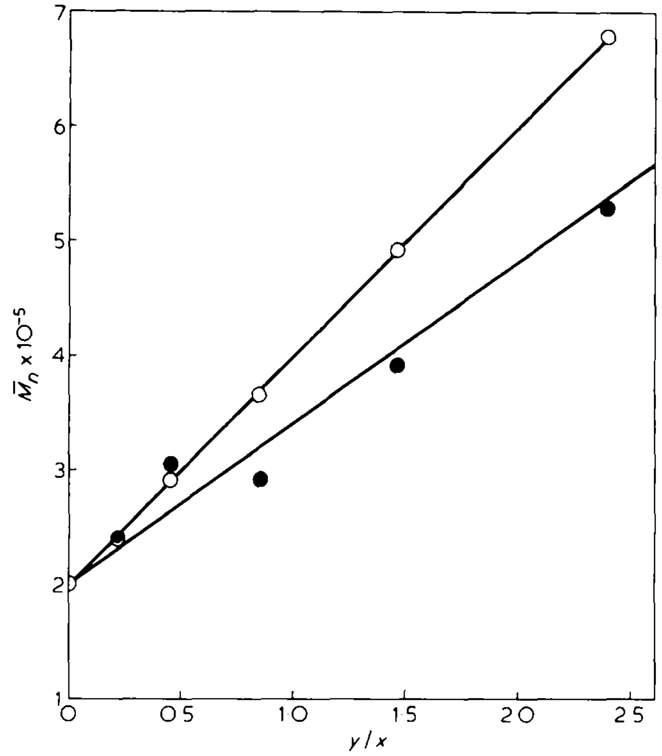


Figure 3 Number average molecular weights, $\bar{M}_n$ of the series-1 graft copolymers as a function of the ratio Y/X. ○, Predicted molecular weight, $\bar{M}_n$ (cal); ●, observed molecular weight, $\bar{M}_n$ (obs)

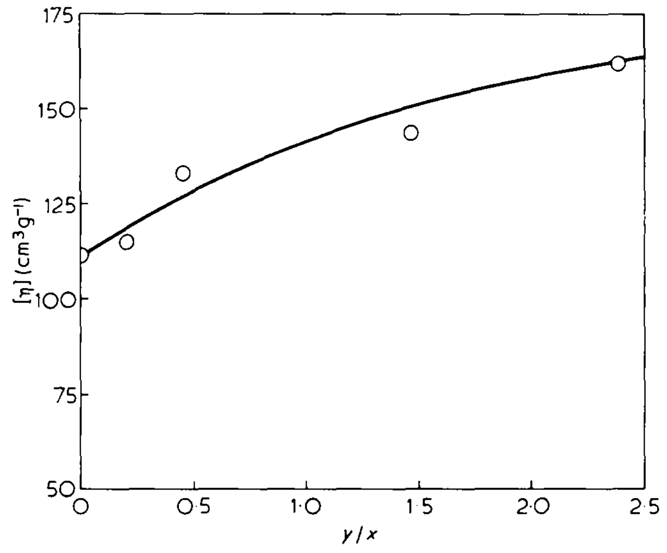


Figure 4 Limiting viscosity numbers of the series-1 graft copolymers, measured in toluene at 30°C, as a function of the ratio Y/X

solution in pure carbon tetrachloride solution, *Figure 5*, sample II. Solutions of the graft copolymers in toluene cyclohexane mixtures became colloidal as the % non-solvent was increased and viscosity measurements could not be made beyond the composition corresponding to the final points in *Figure 6*. The chain dimensions of the low molecular weight polystyrene sample PS-1 remained almost unaffected by the solvent composition, in toluene cyclohexane at 40°C as indicated in *Figure 6*. Similar behaviour could be expected for a low molecular weight polystyrene in benzene–carbon tetrachloride.

The behaviour of the graft copolymers in the mixed solvents may be explained as due to the formation of monomolecular micelles. As the amount of selective precipitant for the backbone is increased, the backbone collapses but is kept in solution by the surrounding solvated grafts. This behaviour is in agreement with some previous studies on graft copolymers[17,18]. However, in some other studies[19,20], it was observed that $[\eta]$ first showed an increase with increase in the amount of selective non-solvent added, followed by a sharp decrease with higher % non-solvent. This initial increase in $[\eta]$, due to an increase in molecular dimensions, was related to an increased repulsion between unlike chain segments. Such polymer polymer interaction, associated with changes in conformation, was shown to be solvent-dependent[19]. In the present study, this behaviour was observed to a small extent for sample 1, as shown in *Figure 5*.

The differential scanning calorimetry measurements using graft copolymers with short PS branches, showed two diffuse T_gs, indicating partial phase separation. As the % PS in the graft copolymers increased, the lower glass transition temperature T_{gA}, characteristic of PECH segments, became more diffuse and also showed a slight increase, as shown in *Figure 6*, sample I. The upper glass transition temperature, T_{gB}, characteristic of polystyrene grafts, became sharper with increase of % PS in the graft copolymer but its value progressively decreased. Preheating the samples at 105°C before thermal analysis gave a marked change in the T_{gB} values, as shown in *Figure 6*. These results indicate phase separation but the behaviour of the higher T_g, associated with the polystyrene phase, requires further detailed investigation.

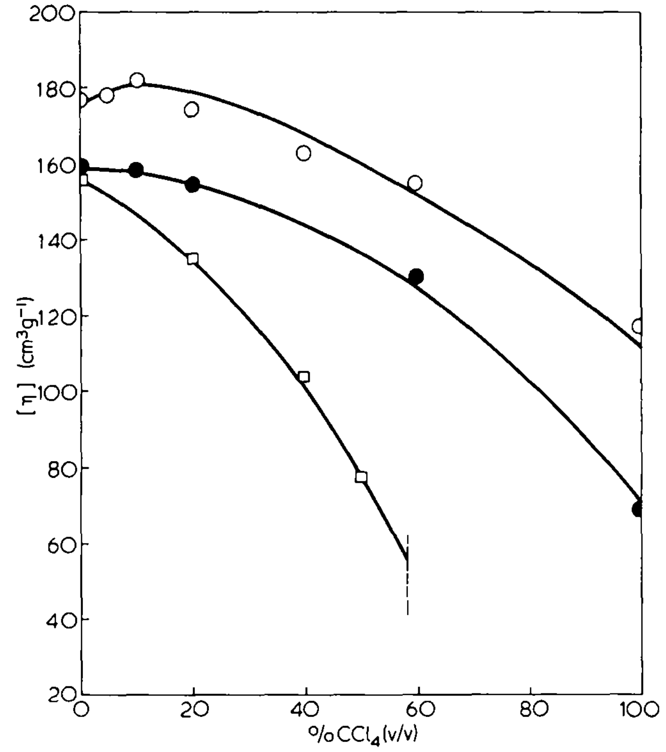


Figure 5 Limiting viscosity numbers of P(ECH–*g*–S)s and homopolymer PECH in benzene–carbon tetrachloride solvent mixtures at 25°C as a function of solvent composition. ○, Sample I, P(ECH–*g*–S) having $\bar{M}_w$ = 22.53 × 10^5, % PS w/w content = 68.0, $\bar{M}_w$ (PS grafts) = 6.22 × 10^3. ●, Sample II, P(ECH–*g*–S) having $\bar{M}_w$ = 11.82 × 10^5, % PS w/w content = 69.6, $\bar{M}_w$ (PS grafts) = 11.40 × 10^4. □, Sample III, PECH having $\bar{M}_w$ = 14.33 × 10^5. Vertical dotted line represents solvent composition at which PECH just precipitates out of solution

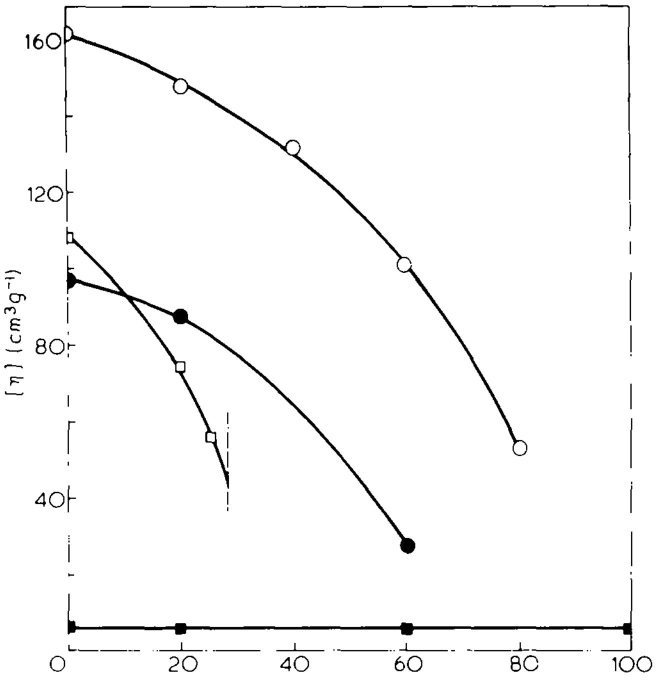


Figure 6 Limiting viscosity numbers of P(ECH–*g*–S)s and homopolymers, PECH and PSCOOH in toluene–cyclohexane solvent mixtures at 40°C, as a function of solvent composition. ○, Sample I, P(ECH–*g*–S) having $\bar{M}_w$ = 24.30 x 10⁵, % PS w/w content = 70.7, $\bar{M}_w$ (PS grafts) = 3.34 x 10³. ●, Sample II, P(ECH–*g*–S) having $\bar{M}_w$ = 9.41 x 10⁵, % PS w/w content = 46.1, $\bar{M}_w$ (PS grafts) = 3.34 x 10³. □, Sample III, PECH having $\bar{M}_w$ = 11.13 x 10⁵. ■, Sample IV, PSCOOH sample PS–1 having $\bar{M}_w$ = 3.34 x 10³. Vertical broken line represents solvent composition at which PECH just precipitates out of solution

The measured T_g value for the PSCOOH sample of number average molecular weight 2.41×10^3 was 82 C as shown in *Figure 7*. This relatively high value of T_g may be explained to some extent if the PSCOOH molecules form H-bonded dimers in the solid state. Slight instrumental instability was observed during thermal analysis of all pre-heated samples above 60 C.

A plot of tan δ as a function of temperature, for some P(ECH-*g*-S)s also showed two transitions, indicating partial phase separation. The sharpness of the transition points again depended on the graft copolymer composition. Thus a graft copolymer ($\bar{M}_n = 3.89 \times 10^5$) containing 59.5% w/w PS of $\bar{M}_n$ equal to 2.41×10^3 showed a weak broad transition at about 0 5 C and a sharp transition at 62.5 C.

The electron micrograph of a P(ECH-*g*-S) sample ($\bar{M}_n = 2.42 \times 10^5$), containing short PS grafts ($\bar{M}_n = 2.41 \times 10^3$), showed phase separation with irregularly dispersed domains (black spots) of unequal sizes.

Graft copolymers formed by using $PSCH_2CH(CH_3)S^-K^+$

Grafting of polystyrene onto PECH, using $PSCH_2CH(CH_3)S\ K^+$, was expected to be of relatively high efficiency due to the very high nucleophilicity of the mercapto end-group. In two grafting experiments with *R* equal to 5.61×10^{-3} and 11.70×10^{-3}, the % grafting efficiency was found to be 54% and 67%, respectively, for a reaction time of 1 h at 40 C. The graft copolymers also underwent cleavage with *f* values of 14.7 and 23.1, respectively. The % grafting efficiency values achieved in these experiments were greater than those achieved using

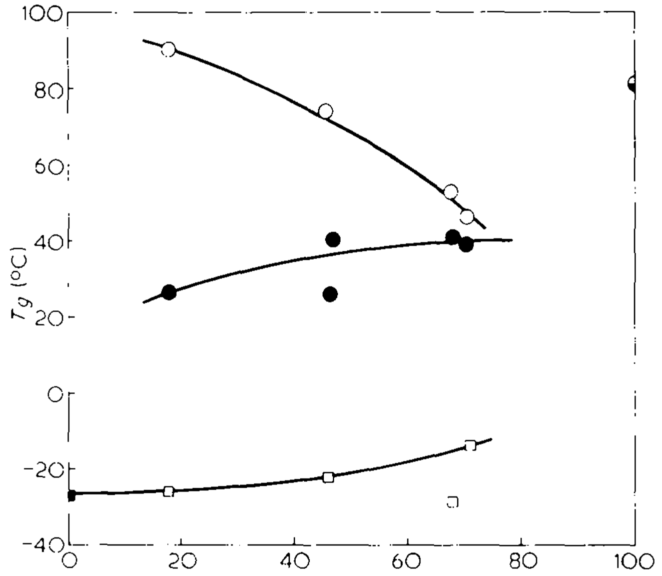


Figure 7 Glass transition temperatures of P(ECH–*g*–S)s containing short PS grafts as a function of % PS w/w. □, T_{gA}, lower T_g characteristic of PECH segments, unchanged by preheating. ○, T_{gB}, upper T_g characteristic of PS segments. ●, T_{gB}, upper T_g characteristic of PS segments in preheated samples. □, T_g of pure PECH; $\bar{M}_n$ = 1.98 x 10⁵. ●, T_g of pure PSCOOH; $\bar{M}_n$ = 2.41 x 10³

PSCOO for 1 h at the higher temperature of 60 C.

Modification of PECH. In the modification reaction involving potassium phenyl acetate, $C_6H_6CH_2COO^-K^+$, in DMF, with a molar ratio of $C_6H_5CH_2COO^-$ to Cl equal to 0.73, A was 30% and **B** was 41%, after 10 h at 60 C.

Substitution of Cl from PECH in DMF by $C_6H_5CH_2S^-$ groups was found, on the contrary, to give *B* values of 100, after 10 h at 60 C. Thus in an experiment with a molar ratio of $C_6H_5S\ Na$ to Cl of 0.50, *A* was 50% and *B* was 100%. In another experiment, using a molar ratio equal of 1.51, *B* was 100% indicating that complete substitution had occurred. The relatively hgih reactivity of the thiophenoxide ion arises from the polarizability of the electron cloud around the sulphur atom. The observed molecular weights of the PECH samples modified with $C_6H_5CH_2COO$ and C_6H_5S groups agreed within 10% with the calculated values, indicating that only low degradation of PECH was induced by these ions.

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