

Graft Polymerization of Propylene Sulfide on Crosslinked Polystyrene

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Synopsis

Sulfur containing graft polymers that may be of interest as polymeric transfer agents were synthesized. Graft polymerization of propylene sulfide on crosslinked polystyrene beads was investigated; both crosslinked polystyrene and its chloromethylated derivative were grafted. Crosslinked polystyrene was metallated by BuLi-TMEDA and was used to initiate anionic graft polymerization of propylene sulfide. Graft polymers of high polypropylene sulfide content corresponding to 10 mmol s/g were obtained. The grafted polypropylene sulfide was evenly distributed across the bead cross section. No change in bead surface characteristics was observed. Grafting on chloromethylated polystyrene beads was achieved by reaction between the chloromethylene groups with sulfide groups of preformed polypropylene sulfide, and with terminal sodium thiolate groups of living polypropylene sulfide.

INTRODUCTION

The first systematic investigation of anionic polymerization of propylene sulfide, undertaken by Sigwalt et al.,^{1,2} showed clearly that anionic living polymerization of propylene sulfide can be used for the synthesis of well-defined block and graft polymers. Preparation, characterization, and properties of block and graft polymers derived from propylene sulfide and diene monomers, vinyl monomers, polyurethanes, nylon, and cellulose were reported in literature. Block polymers derived from butadiene and isoprene were prepared by anionic polymerization technique.^{3,4} Block polymers poly(α -methylstyrene)-poly(propylene sulfide)-poly(α -methylstyrene), which are of interest as thermoplastic elastomers, were synthesized using ethyllithium as an initiator and phosgene to couple the active lithium thiolate chain ends.⁵ Block copolymers of poly(propylene sulfide)-polystyrene were prepared by reaction of living polystyrene, initiated by butyllithium, sodium naphthalene,⁶ or sodium biphenyl,⁷ with propylene sulfide. Similarly graft polymers of vinyl pyridine and propylene sulfide were prepared by anionic polymerization from the corresponding monomers.⁸ Anionic graft polymerization of propylene sulfide on polyurethane was reported in literature.⁹ Polyurethane based on methylene bis(4-phenylisocyanate) and ethylene glycol was metallated by sodium hydride in *N,N*-dimethylformamide. The metallated polymer was used to initiate anionic graft polymerization of acrylonitrile, ethylene, and propylene sulfide. Compatible interpenetrating polymer networks systems, of improved heat resistance and mechanical properties have been obtained by two-stage polymerization of a mixture of diisocyanate with various different polar monomers, among them

* Part of Ph.D. thesis to be submitted to the Senate of the Hebrew University.

propylene sulfide.^{10,11} Poly(propylene sulfide-*g*-cellulose) was reported in literature. Treating of activated cellulose with ethylene sulfide or propylene sulfide in the presence of potassium, sodium, and ammonium sulfide or hydrosulfide lead to the formation of the corresponding graft polymer.¹² Anionic graft polymerization of propylene sulfide on cotton fabric and cellulosic membranes was reported.^{13,14} Similarly anionic graft polymerization of propylene sulfide on metallated nylon 6 fibers was achieved.¹⁵ The donor properties of sulfide bonds in the graft polymers of polypropylene sulfide (PPS) were utilized to absorb by complexation iodine^{13,14} as well as heavy metal salts.¹³⁻¹⁵ With poly(propylene sulfide-*g*-cellulose)^{13,14} almost complete participation of the sulfide groups in the complexation reaction has been achieved.

The donor properties of the sulfide group present in a polymer were used by Crosby et al.¹⁶⁻¹⁸ for the preparation of polymeric reagents. Such reagents were classified¹⁹ as polymeric transfer agents. These polymers were based on crosslinked polystyrene which was substituted by sulfide groups. The corresponding insoluble polymeric thioanisole was prepared and converted to its chlorosulfonium chloride derivative by reaction with chlorine.¹⁶ In that form it was used as an effective mild oxidation reagent of primary and secondary alcohols. Due to a polymeric immobilization effect, the polymer selectively monooxidized dialcohols. This polymer was also used for homologation of alkyl iodides.¹⁷ Chloromethylated crosslinked polystyrene was used to prepare polymeric benzyl methyl sulfide.¹⁸ This polymer was converted to its borane complex by reaction with diborane at -196°C . The borane complexed polymer was employed in hydrogenation and hydroboration reactions.

Degree of functionalization of such polymers is dependent on and limited by the extent of substitution of the crosslinked polymer. High functionalization can be reached only by a high degree of substitution, which some times is hard to achieve and, when achieved, may alter the nature of the crosslinked polymer. Values of 1-2 mmol/g are frequently reported as high loading values.¹⁹ A much higher degree of functionalization at a low degree of substitution can be achieved by graft polymerization. Graft polymerization of low molecular weight monomer containing the required functional group will lead to the formation of a graft polymer in which, at minimal degree of substitution, high degree of functionalization is reached. Due to the low degree of substitution required for efficient grafting, the crosslinked polymer used as support for the polymeric reagent will remain practically intact. Degree of functionalization will be limited only by the extent of incorporation of grafted side chains in the crosslinked polymer. It can be expected that degree of functionalization via grafting will be much higher than that obtained even at complete substitution of the polymeric support with a low molecular weight substituent. Graft polymers can be used as polymeric reagents in which high degree of functionalization is reached with minimal alteration of the crosslinked polymeric support.

In the present work we investigated the graft polymerization of propylene sulfide on crosslinked polystyrene and chloromethylated crosslinked polystyrene, commonly used as support for polymeric reagents.¹⁹ Anionic graft polymerization and graft polymerization by reaction between preformed

polymers were investigated. Such graft polymers of high polysulfide content in which donor properties of the sulfide bonds are combined with chemical and physical properties of the crosslinked polystyrene may be of interest as polymeric transfer reagents of versatile use.

EXPERIMENTAL

Materials. Propylene sulfide (Fluka) was redistilled from calcium hydride before use. Boron trifluoride ethyl etherate (Fluka), *N,N,N,N'*-tetramethylene diamine (TMEDA) (Eastman) were redistilled before use. Toluene, benzene, and hexane (Frutarom) were dried with sodium and distilled before use. Tetrahydrofuran (Frutarom) was dried by distillation from its sodium benzophenone solution. Sodium naphthalene solution was prepared by reaction of sodium with naphthalene in THF. *n*-Butyllithium 2*M* in hexane (Aldrich), crosslinked polystyrene-copolymer of 98% styrene + 2% divinylbenzene 200–400 mesh, and chloromethylated copolymer of 99% styrene + 1% divinylbenzene, 1.04 mmol Cl/g, 200–400 mesh (Fluka) were used. Crosslinked polymers were extracted with chloroform and methanol and dried before use.

Graft polymerization Reactions. Reactions were carried out under argon in a closed flask equipped with a self-sealing rubber cap for the introduction of reagents by syringes. The reactions flask was flamed in vacuum and flushed with argon. When necessary, glove box was used. Homopolypropylene sulfide was removed by extraction with chloroform in soxhelt apparatus, and was isolated by precipitation in methanol. Elemental analysis, and NMR spectra of the extracted polymer showed that in all graft polymerization reactions pure homopolypropylene sulfide was extracted.

Reaction between BuLi-TMEDA and Crosslinked Polystyrene. To crosslinked polystyrene, *n*-butyllithium, 2*M* solution in hexane was added followed by an equivalent amount of TMEDA. Reaction mixture was kept at 35°C under constant stirring for 6 h. The lithiated polymer was isolated by filtration and was washed with toluene (5 × 10 mL) and petroleum ether (5 × 10 mL). The polymer was dried in vacuum at room temp. The lithium content of the polymer was determined by titration after hydrolysis.

Graft Polymerization of Propylene Sulfide on Crosslinked Polystyrene. Propylene sulfide (2.85 g) was added to lithiated polystyrene (0.5 g, 1.8 mmol Li/g). Polymerization was carried out at room temp under constant stirring. After 24 h, 5% acetic acid in methanol (5.0 mL) was added. The product was washed with methanol, dried, and weighed; 3.34 g were obtained corresponding to 100% total polymerization yield. Homopolymer was removed by extraction. The graft polymer was washed with water and methanol and dried in vacuum on P₂O₅ for 24 h at 45°C. The graft polymer contained 74% PPS corresponding to 50% graft polymerization yield. Similar procedure was applied when graft polymerization was carried out in solution. The solvent (4 mL) was added to the crosslinked polymer prior to monomer addition.

Graft Polymerization of Preformed Poly(propylene Sulfide) on Chloromethylated Crosslinked Polystyrene. To chloromethylated polystyrene (1.0 g, 3.8% Cl) propylene sulfide (4.0 g) was added. The crosslinked polymer was allowed to swell in the monomer for 10 min. Polymerization of propylene sulfide was initiated by addition of (0.2 mL) boron trifluoride etherate. Polymerization mixture was kept at 25°C, and was left for 18 h under constant stirring. In order to react the preformed polypropylene sulfide with chloromethylated crosslinked polystyrene, the reaction flask was kept at 80°C. The homopolymer present was removed by extraction with chloroform.

Graft polymerization of Propylene sulfide on Chloromethylated Polystyrene. To chloromethylated polystyrene (1.0 g, 3.8% Cl) propylene sulfide (4.0 g) was added. The polymer was allowed to swell for 10 min in the monomer and sodium naphthalene 0.6M solution in THF (1 mL) was added. Reaction mixture was left at room temp overnight under constant stirring. The polymer was washed with 5% acetic acid in methanol; 5.0 g were recovered, corresponding to 100% polymerization yield. The homopolymer was extracted with chloroform. The isolated graft polymer contained 2.0% Cl and 10.0% S corresponding to 23.1% PPS content and 7.5% graft polymerization yield.

Graft Polymerization of Propylene Sulfide on Hydroxymethylated Crosslinked Polystyrene. Chloromethylated polystyrene (1.0 g, 3.8% Cl) was allowed to react with 4% NaOH solution in DMSO:water (95:5) at 100°C, overnight. The polymer was washed with methanol:water (1:1) and dried; chlorine analysis 0.5% was found. The polymer was allowed to react for 1 h with 2*N* lithium methoxide solution (5 mL). Excess of lithium methoxide was removed by filtration. The polymer was washed by dry hexane. Propylene sulfide (4.0 g) was added and reaction mixture was left overnight at room temp under constant stirring. Crude polymer 2.1 g was isolated corresponding to 27.5% polymerization yield. After extraction of the homopolymer, graft polymer of 10.0% S corresponding to 23.1% PPS content and 7.5% graft polymerization yield was obtained.

RESULTS AND DISCUSSION

Graft polymerization of propylene sulfide on crosslinked polystyrene was studied, using copolymer 98% styrene + 2% divinylbenzene and chloromethylated copolymer 99% styrene + 1% divinylbenzene. Different graft polymerization techniques were applied for grafting on the two crosslinked polymers.

Graft Polymerization of Propylene Sulfide on Crosslinked Polystyrene. Anionic graft polymerization of propylene sulfide on crosslinked polystyrene was studied. Carbanions formed on the polystyrene were used to initiate anionic graft polymerization of propylene sulfide. Metallation of polystyrene was reported in literature. Halogenation in the presence of ferric chloride or thalic acetate followed by treatment with butyllithium in THF lead to the formation of a lithiated polystyrene.²⁰ Mercuration of polystyrene followed by treatment with butyllithium leads to the formation of the same polymer.²¹ Polystyrene was also metallated directly by

TABLE I
Graft Polymerization of Propylene Sulfide on Crosslinked Polystyrene—Time Dependence^a

| Reaction time (min) | Polymerization yield | | | Graft polymer | | | PPS content (%) |
|---------------------|----------------------|----------|-----------|---------------------|--------------------|----------|-----------------|
| | Graft (%) | Homo (%) | Total (%) | Weight increase (%) | S in graft polymer | | |
| | | | | | (%) | (mmol/g) | |
| 4 | 44 | 32 | 76 | 247 | 30.8 | 9.60 | 71.2 |
| 15 | 48 | 41 | 89 | 271 | 31.6 | 9.87 | 73.1 |
| 60 | 50 | 49 | 99 | 285 | 32.0 | 10.2 | 74.0 |
| 1440 | 50 | 50 | 100 | 285 | 32.0 | 10.2 | 74.0 |

^a Lithiated crosslinked polystyrene (0.5 g, 1.8 mmol Li/g) was allowed to react with propylene sulfide (3.0 mL) at 25°C.

reaction with butyllithium-*N,N,N',N'*-tetramethylethylenediamine (BuLi-TMEDA).²² This metallation procedure was applied recently also to crosslinked polystyrene.²³

In the present work the BuLi-TMEDA reagent was used for the preparation of lithiated crosslinked polystyrene. The lithiated polymer was used to initiate anionic graft polymerization of propylene sulfide. Time dependence of anionic graft polymerization on lithiated 2% divinylbenzene-styrene copolymer was determined. Unreacted lithiation reagent was removed by extraction prior to the addition of the propylene sulfide. Grafting was carried in bulk (Table I) and in THF (Table II). Polymerization was terminated by 5% acetic acid in methanol. Graft polymerization was accompanied by homopolymerization. Traces of unextractable BuLi-TMEDA are most probably responsible for initiation of homopolymerization. The homopolymer formed was removed by extraction with chloroform. Anionic graft polymerization of propylene sulfide on crosslinked polystyrene is a fast reaction. The PPS content of the graft polymer after 4 min (71.2%) corresponds to 92% of the final PPS content (74%) at 100% conversion. Graft polymerization in THF lead to similar results. Graft polymerization yield is less dependent on reaction time. Longer reaction time leads to a relative increase in homopolymerization yield. The graft polymers obtained are of high functionality, values of 10 mmol S/g polymer were reached.

Graft polymerization carried out under similar reaction conditions in

TABLE II
Graft Polymerization of Propylene Sulfide in THF Crosslinked Polystyrene—Time Dependence^a

| Reaction time (min) | Polymerization yield | | | Graft polymer | | | PPS content (%) |
|---------------------|----------------------|----------|-----------|---------------------|--------------------|----------|-----------------|
| | Graft (%) | Homo (%) | Total (%) | Weight increase (%) | S in graft polymer | | |
| | | | | | (%) | (mmol/g) | |
| 4 | 30 | 45 | 75 | 171 | 27.3 | 8.53 | 63.2 |
| 15 | 35 | 52 | 87 | 195 | 28.6 | 8.93 | 66.4 |
| 60 | 36 | 60 | 96 | 203 | 28.9 | 9.00 | 67.0 |
| 1440 | 38 | 62 | 100 | 217 | 29.6 | 9.25 | 68.7 |

^a Lithiated crosslinked polystyrene (0.5 g, 1.8 mmol Li/g) was allowed to react in THF (4 mL), with propylene sulfide (3.0 mL) at 25°C.

TABLE III
Graft Polymerization of Propylene Sulfide on Crosslinked Polystyrene in Different Solvents^a

| | Polymerization yield | | | Graft polymer | | | PPS content (%) |
|-------------|----------------------|----------|-----------|---------------------|--------------------|----------|-----------------|
| | Graft (%) | Homo (%) | Total (%) | Weight increase (%) | S in graft polymer | | |
| | | | | | (%) | (mmol/g) | |
| — | 50 | 50 | 100 | 271 | 31.6 | 9.87 | 73.1 |
| Benzene | 50 | 50 | 100 | 285 | 32.0 | 10.0 | 74.0 |
| Cyclohexane | 32 | 46 | 78 | 178 | 27.7 | 8.65 | 64.0 |
| THF | 35 | 61 | 96 | 195 | 28.6 | 8.93 | 66.1 |

^a Lithiated crosslinked polystyrene (0.5 g, 1.8 mmol Li/g) was allowed to react, in a solvent (4 mL) with propylene sulfide (3.0 mL) at room temp for 24 h.

different solvents are reported in Table III. Graft polymers of high PPS content were obtained. Results obtained in benzene were similar to those obtained in bulk polymerization.

Reaction carried out in cyclohexane and THF led to a decrease in graft polymerization yield, an increase in homopolymerization yield, and the formation of graft polymers with relatively lower PPS content. Graft polymerization of propylene sulfide can be carried out in bulk as there is no advantage in using a solvent. The influence of the degree of lithiation of the crosslinked polymer on graft polymerization yield is reported in Table IV. Lithiated polymers of different lithium content were prepared by reaction with different amounts of BuLi-TMEDA. The PPS content of the graft polymer increased with degree of lithiation; under these conditions graft polymerization was favored over homopolymerization.

Because of the nature of anionic graft polymerization of propylene sulfide it is expected that the increased amount of monomer available for polymerization will lead to increase in PPS content of the graft polymer. Graft polymerization in the presence of varying amounts of propylene sulfide was carried out, under conditions leading to 100% total polymerization yield (Table V). Values up to 76.3 mmol/g polymer correspond to complete solution of the monomer in the crosslinked polymer. Increase in amount of monomer available for polymerization leads to an increase in the PPS content of the graft polymer till final value of 74% is reached. The higher PPS content reached with increase in monomer concentration was accompanied by a decrease in graft polymerization yield and an increase in homopolymerization yield.

Graft Polymerization of Propylene Sulfide on Chloromethylated Crosslinked Polystyrene. Chloromethylated polystyrene was used for the preparation of the corresponding PPS graft polymer. The reactive chloromethylene group can react with sulfide groups of a preformed PPS to yield the corresponding sulfonium groups. Such reactions will lead to the formation of a graft polymer. Sulfonium salts are relatively unstable and upon heating will undergo nucleophilic substitution or 1,2 elimination. The choice between these two modes of reactions depends upon the relationship between proton and carbon nucleophilicity for the nucleophile in question. Either substitution or elimination will yield a graft polymer in which the

TABLE IV
Graft Polymerization of Propylene Sulfide on Crosslinked Polystyrene at Different Degrees of
Lithiation^a

| BuLi- TMEDA (mmol/g polymer) | Polymerization yield | | | | Graft polymer | | | PPS content (%) |
|---------------------------------------|--|--------------|-------------|--------------|---------------------------|---------------------------|----------|-----------------------|
| | L ^b in polymer (mmol/g) | Graft (%) | Homo (%) | Total (%) | Weight increase (%) | S in graft polymer (%) | (mmol/g) | |
| 8.5 | 1.8 | 50 | 50 | 100 | 284 | 32.0 | 10.0 | 74.0 |
| 6.3 | 1.3 | 46 | 51 | 97 | 257 | 31.1 | 9.7 | 71.9 |
| 4.3 | 0.8 | 37 | 54 | 91 | 206 | 29.2 | 9.1 | 67.3 |
| 1.5 | 0.3 | 11 | 46 | 57 | 59 | 16.0 | 5.0 | 37.0 |

^a Crosslinked polystyrene (0.5 g) was allowed to react with BuLi, 2M solution in hexane in the presence of equivalent amount of TMEDA for 5 h at 55°C. Excess of BuLi-TMEDA was removed and propylene sulfide (3.0 mL) was added. Graft polymerization was carried out at room temp for 24 h.

^b Determined by titration after hydrolysis.

TABLE VI
Graft Polymerization of Preformed Poly(propylene Sulfide) on Chloromethylated Crosslinked Polystyrene^a

| Reaction time (h) | Graft polymer analysis | | Graft polymer weight increase (%) | PPS in graft polymer (%) | S in graft polymer (mmol/g) | Remaining Cl in graft polymer (%) ^b |
|-------------------|------------------------|--------|-----------------------------------|--------------------------|-----------------------------|--|
| | S (%) | Cl (%) | | | | |
| 0 | 6.0 | 3.10 | 16.1 | 13.9 | 1.87 | 95.2 |
| 2 | 12.2 | 2.51 | 39.3 | 28.2 | 3.80 | 92.2 |
| 4 | 13.5 | 2.34 | 45.2 | 31.2 | 4.20 | 89.1 |
| 6 | 14.4 | 1.67 | 50.0 | 33.3 | 4.50 | 66.3 |
| 11 | 17.2 | 1.38 | 66.3 | 39.8 | 5.37 | 61.4 |
| 15 | 19.0 | 1.00 | 78.5 | 43.9 | 5.93 | 47.5 |
| 30 | 24.6 | 0.60 | 132.3 | 57.0 | 7.70 | 37.6 |
| 110 | 23.8 | 0.50 | 122.3 | 55.0 | 7.40 | 29.7 |

^a Graft polymerization was carried out by keeping preformed PPS (4.0 g) in chloromethylated crosslinked polystyrene (1.0 g, 1.04 mmol Cl/g, 3.80% Cl) at 80°C.

^b % of the original chlorine content.

may be assumed that, in the graft polymers obtained, most of the polysulfide side chains are attached to the crosslinked polymer by a sulfide bond and the residual chlorine (0.5%) present in the polymer is of unreacted chloromethylene groups. In this case the molecular weight of the grafted polysulfide can be calculated from the graft polymer polysulfide content and from the decrease in the chlorine analysis. A molecular weight of 1550 was calculated. The molecular weight of the preformed polymer which was extracted from the crosslinked polystyrene prior to graft polymerization was determined viscosimetrically.²⁵ A value of 20,900 was found. The lower molecular weight of the grafted polypropylene supports the suggested graft polymerization reactions sequence.

Graft polymerization of polypropylene sulfide on chloromethylated crosslinked polystyrene can be achieved by reaction between thiolate terminal groups of living PPS and chloromethylene groups of the crosslinked polymer. The synthesis of graft polymer by this technique was investigated. In order to minimize diffusion problems of high molecular weight polysulfide, the propylene sulfide was introduced into the crosslinked polymer prior to polymerization. Polymerization was initiated by sodium naphthalene. The use of this initiator guaranteed two terminal active groups per polysulfide chain. Reaction between thiolate end groups of PPS and chloromethylene groups on the crosslinked polystyrene led to the formation of graft polymer. After extraction of unreacted PPS, graft polymer of 23.1% PPS content was obtained. Graft polymerization was accompanied by decrease of 47% in original chlorine content. This decrease is probably due both to reaction with living PPS and sodium naphthalene itself. Therefore, molecular weight of the grafted side chains cannot be calculated from the decrease in original chlorine analysis of the graft polymer.

Chloromethylated crosslinked polystyrene was also used for initiating anionic graft polymerization of propylene sulfide. The chloromethylated crosslinked polystyrene was converted to the analogous alcohol and its

TABLE VII
Beads' Diameter after Graft Polymerization

| Polymer | S (%) | Beads' diameter ^a (μm) |
|---|-------|-----------------------------------|
| Chloromethylated crosslinked polystyrene | 0.0 | 482 ± 66 |
| Grafted chloromethylated crosslinked polystyrene ^b | 10.0 | 525 ± 76 |
| Grafted chloromethylated crosslinked polystyrene ^c | 24.6 | 600 ± 101 |
| Crosslinked polystyrene | 0.0 | 177 ± 97 |
| Grafted crosslinked polystyrene | 13.0 | 229 ± 79 |
| Grafted crosslinked polystyrene | 26.9 | 314 ± 124 |

^a Average value of 50 measurements at magnification of × 4000.

^b Graft polymer prepared by the sodium naphthalene procedure.

^c Graft polymer prepared by reaction with preformed PPS.

alcoholate was used to initiate graft polymerization of propylene sulfide. Graft polymer of 23.1% PPS content was obtained.

The different graft polymerization procedures investigated led practically to the same graft polymer. Graft polymerization of propylene sulfide on crosslinked polystyrene using BuLi-TMEDA procedure is the recommended one. This procedure is the simplest, leads to the best graft polymerization yield and to the highest PPS content of the graft polymer.

Scanning Electron Microscope (SEM) Examination. The structure of macromolecular network has an important role in ion exchange process. Ion exchange kinetics and ion selectivity can be changed through modification of the network.^{26,27} It was interesting to see whether change in shape and surface characteristics of the polymer beads took place during graft polymerization, and to what extent is the grafted PPS distributed evenly inside the polymer bead. Scanning electron micrographs of grafted ungrafted crosslinked polystyrene were compared (Fig. 1). No change in beads' shape was observed even at the highest PPS content. Similar micrographs were obtained for grafted chloromethylated crosslinked polystyrene. Graft polymerization led to an increase in beads' diameter as determined from SEM micrographs (Table VII). Surface characteristics of the grafted beads did not change, except for graft polymers of chloromethylated crosslinked

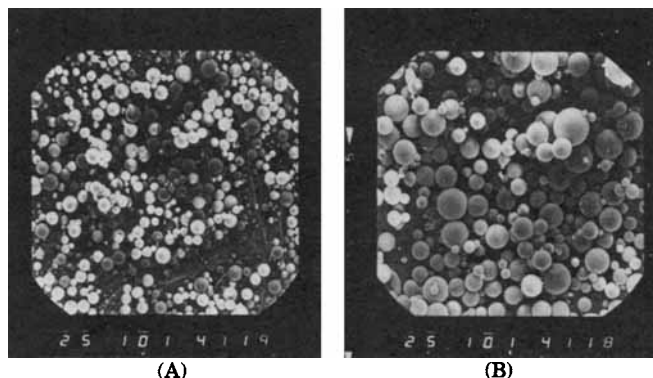


Fig. 1. Scanning electron microscope picture of grafted and ungrafted crosslinked polystyrene beads: (A) ungrafted crosslinked polystyrene; (B) graft polymer, 29.6% S, 68.7% PPS content.

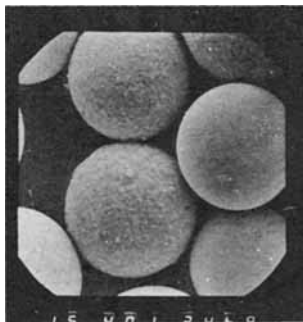


Fig. 2. Scanning electron microscope picture of chloromethylated crosslinked polystyrene grafted with preformed PPS, 24.6% S, 57.0% PPS content.

polystyrene of the highest PPS content, which were prepared by reaction with preformed PPS. In some of these graft polymer beads surface roughness was developed (Fig. 2). Inspection of the graft polymer beads at much higher magnification ($\times 10,000$) showed the same phenomena. Scanning electron micrographs were taken of fractured grafted and ungrafted beads. Fractured beads were obtained by cutting into small section blocks of polystyrene in which graft polymer beads were embedded. The beads were recovered by removing the polystyrene by extraction. No change in beads internal structure was observed. PPS distribution in the beads' cross section was determined by SEM from reflecting count at 38 kV using an electron beam of 2280 eV which detects the presence of sulfur. The bead cross section was scanned along its radius. Five counts were taken for each quarter of the radius. This procedure was repeated with three fractured beads. The average values are reported in Figure 3. Three different graft polymers were compared. Graft polymer prepared from crosslinked polystyrene and two graft polymers prepared from chloromethylated polystyrene, one by reaction with preformed PPS and another by anionic polymerization of propylene sulfide. It can be seen that in the graft crosslinked polystyrene beads, even at the highest PPS content, the PPS is practically evenly distributed

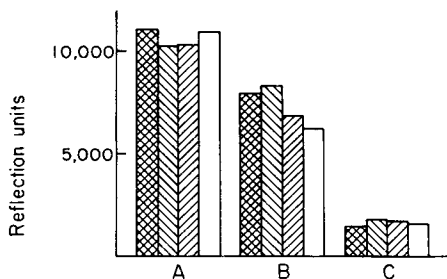


Fig. 3. PPS distribution in graft polymer beads' cross section: (A) graft polymer prepared by BuLi-TMEDA procedure, 32% S; (B) graft polymer prepared using preformed PPS, 24.6% S; (C) graft polymer prepared using sodium naphthalene, 10.0% S. (□) Reflection units counted for 60 s at 0-25% of beads' radius; (▨) reflection units counted for 60 s at 25-50% of beads' radius; (▩) reflection units counted for 60 s at 50-75% of beads' radius; (▧) reflection units counted for 60 s at 75-100% of beads' radius.

along the bead cross section. Some uneven distribution of the grafted PPS, due to diffusion problem, can be seen in graft polymer beads prepared by reaction with a preformed polymer.

The BuLi-TMEDA procedure by which graft polymers of the highest PPS content were prepared led to graft polymer beads in which beads' shape and surface characteristics were not changed. In these graft polymers even at the highest PPS content, the grafted polysulfide was evenly distributed inside the polymer bead.

Financial assistance from Ernst David Bergmann Science Foundation is gratefully acknowledged.

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Received September 7, 1983

Accepted December 19, 1983