

Hydrophilic modification of engineering polymers

T. W. Beihoffer* and J. E. Glass

Polymers and Coatings Department, North Dakota State University, Fargo, North Dakota 58105, USA

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Water-soluble carboxylated polymers were synthesized from engineering polymers via the metallation of poly(oxy-1,4-phenylenesulphonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) and poly(oxy-2,6-dimethyl-1,4-phenylene) with *n*-butyllithium followed by reaction with carbon dioxide. Interactions between lithium sites on the polymer backbones cause the precipitation of highly metallated polymers. Precipitation of PPO occurs at approximately 15% metallation based on polymer repeat unit. Reproducibility problems are encountered with highly metallated, precipitated polymers. An ester-functional comb-type graft copolymer is synthesized via the anionic polymerization of methyl methacrylate (MMA) from metallated sites on PPO. The ester functionalities can be transesterified with hydroxy functional reagents to yield well-defined comb-type graft terpolymers. Transesterification of oligomeric polyethylene glycol onto PPO-MMA yields a comb-type graft terpolymer with nonionic hydrophiles.

(Keywords: engineering polymers; hydrophilic modification; polymerization)

INTRODUCTION

Hydrophilic modifications of synthetic polymers have found use in membrane applications and in the synthesis of water-soluble polymers^{1,2}. Most publications have dealt with the incorporation of ionic hydrophiles on polymers. The incorporation of nonionic hydrophiles on synthetic polymers has received less attention^{3,4}. Poly(oxy-2,6-dimethyl-1,4-phenylene) [poly(phenylene oxide), PPO] (*Figure 1A*) and poly(oxy-1,4-phenylene-sulphonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) [polysulphone, PS] (*Figure 1B*) are examples of engineering polymers that exhibit good chemical and thermal stability. Examples of hydrophilic modification of these polymers are the sulphonation of PS and PPO^{1,5,6} and the carboxylation of PPO⁷. Polyphenylene oxide reacts with *n*-butyllithium to yield a metallated polymer⁷. The lithium sites on the polymer were found to react with carbon dioxide to yield a carboxylated polymer and to initiate anionic polymerization of styrene and methyl methacrylate to yield comb-type graft copolymers^{8,9}.

Comb-type graft copolymers can be formed by either growing polymer sidechains from sites along the backbone or by attaching preformed groups to these sites¹⁰. While much has been published on the use of both of these methods to obtain graft copolymers, the combination of these two methods to achieve trigraft comb-type terpolymers has received little attention. This paper details our efforts to use the metallation reaction with PPO and PS to obtain engineering polymers modified with hydrophilic carboxylate groups and nonionic hydrophilic polyethylene glycol groups. Specifically, it details our efforts to obtain well-defined trigraft terpolymers via the anionic polymerization of methyl methacrylate (MMA) from metallated sites on

poly(phenylene oxide) (PPO) followed by transesterification of hydrophilic oligomeric methoxy initiated polyethylene glycol (MPEG) or 3-phenyl-1-propanol on the MMA sidechains.

EXPERIMENTAL

Materials

Poly(oxy-2,6-dimethyl-1,4-phenylene) [poly(phenylene oxide), PPO, $M_w = 64\,000$] and poly(oxy-1,4-phenylene-sulphonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) [polysulphone, PS] were dried in a heated vacuum desiccator at 100°C. Methoxypolyethylene glycol (MPEG, $M_n = 300$) was azeotropically dried with benzene. Methyl methacrylate (MMA) was distilled from calcium hydride; 3-phenyl-1-propanol (3P1P) was distilled under vacuum and stored over molecular sieves. The solvents used were dried and distilled by conventional methods. All other materials used were reagent grade and were used as received. All reactions were conducted under an atmosphere of oxygen-free nitrogen.

Metallation and carboxylation of PPO and PSF

Polysulphone and poly(phenylene oxide) were metallated at room temperature with *n*-butyllithium (*n*BuLi, 1.6 M in hexane) in dry tetrahydrofuran. Carboxylation was effected by the addition of an excess of solid CO₂ to the reaction mixture. After acidification with HCl the product was recovered via precipitation from water. The degree of carboxylation was determined by potentiometric titration.

PPO-MMA graft copolymer

A slight excess of 1,1-diphenylethylene (DPE) was added to the metallated PPO at room temperature and allowed to stir for 10 min. The temperature of the system was lowered to -77°C and MMA was added via syringe.

* Present address: Amoco Production Co., PO Box 3385, Tulsa, OK 74102, USA

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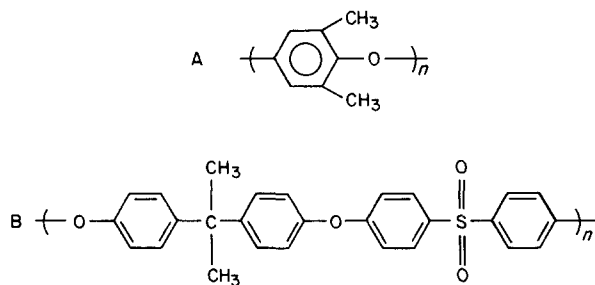


Figure 1 Engineering polymers: (A) poly(phenylene oxide) (PPO); (B) polysulphone (PS)

After 15 min the reaction was terminated by the addition of methanol. The product was recovered via precipitation from water.

PPO-MMA-MPEG graft terpolymer

Potassium naphthalenide was added to dry MPEG in anhydrous toluene to yield the MPEG alkoxide. The temperature of the system was then raised to 110°C and a solution of PPO-MMA in toluene was added dropwise. After 5 h, the temperature was adjusted to allow distillation of the solvent to remove methanol generated by the reaction. The reaction was terminated by the addition of acetic acid and the product was recovered by precipitation in methanol. Crude PPO-MMA-MPEG was purified via extraction with methanol in a Soxhlet extractor.

Transesterification of 3-phenyl-1-propanol on PPO-MMA

The procedure is identical to that of transesterification of MPEG on PPO-MMA except for the substitution of 10 mmol of 3-phenyl-1-propanol (3P1P) for MPEG. The reaction was run once with, and once without, 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6 crown ether) at a molar equivalent to the potassium naphthalenide used. The crown ether was dissolved in the 3P1P prior to the addition of the potassium naphthalenide.

Polymer fractionation

Crude PPO-CO₂H, PS-CO₂H and PPO-MMA reaction products were fractionated in tetrahydrofuran/water solvent/nonsolvent systems by conventional methods¹¹.

Analysis of PPO-MMA

Compositions of the PPO-MMA reaction products, before and after fractionation, were determined from the n.m.r. spectra by comparing areas of peaks specific to protons on the PPO backbone (δ 6.5), DPE (δ 7.17) and MMA (δ 3.6). The sidechain frequency was calculated from the ratio of DPE to PPO (DPE/PPO) and the MMA chain length was determined from the ratio of MMA to DPE (MMA/DPE). The sidechain frequency values have been corrected for metallation on both PPO aromatic ring and methyl groups⁷.

Analysis of PPO-MMA-MPEG

Since the MPEG methylene protons occur at the same position as the MMA ester protons, the amount of MPEG incorporated was calculated by comparing the increase in area of the δ 3.6 adsorption of the PPO-MMA-MPEG over the starting material (PPO-MMA).

The amount of MPEG incorporated is reported with respect to DPE substitution, i.e. MPEG/DPE=1 indicates one MPEG graft per sidechain.

Analysis of PPO-MMA-3P1P

The aromatic protons of the 3-phenyl-1-propanol (3P1P) occur at the same position as the DPE aromatic protons. The amount of 3P1P incorporated was calculated by comparing the increase in the area of the δ 7.17 adsorption of the PPO-DPE-MMA-3P1P over that of the starting material (PPO-MMA). The amount of 3P1P incorporated is reported with respect to DPE substitution (3P1P/DPE).

RESULTS AND DISCUSSION

Carboxylation of PPO and PS

Poly(phenylene oxide) (PPO) was metalated at different levels with *n*-butyllithium by the method of Chalk and Hay⁷ and reacted with an excess of carbon dioxide. The carboxylated polymers were converted to the acid form and titrated to determine per cent carboxylation. Results of the analysis for PPO are illustrated in Figure 2. A linear relationship exists between the amount of *n*-butyllithium (*n* BuLi) used and the amount of metallation obtained up to a *n*BuLi/aromatic (*n*BuLi/Ar) ring ratio of approximately 0.22. At ratios higher than 0.22, associations between the metallated sites result in polymer precipitation. Carboxylation of highly metallated precipitated PPO is complicated by the restricted access of CO₂ to the lithium sites on the polymer. The restricted access results in uneven carboxylation among polymer molecules and the formation of an insoluble fraction due to the reaction of a carboxylated site with a metallated site

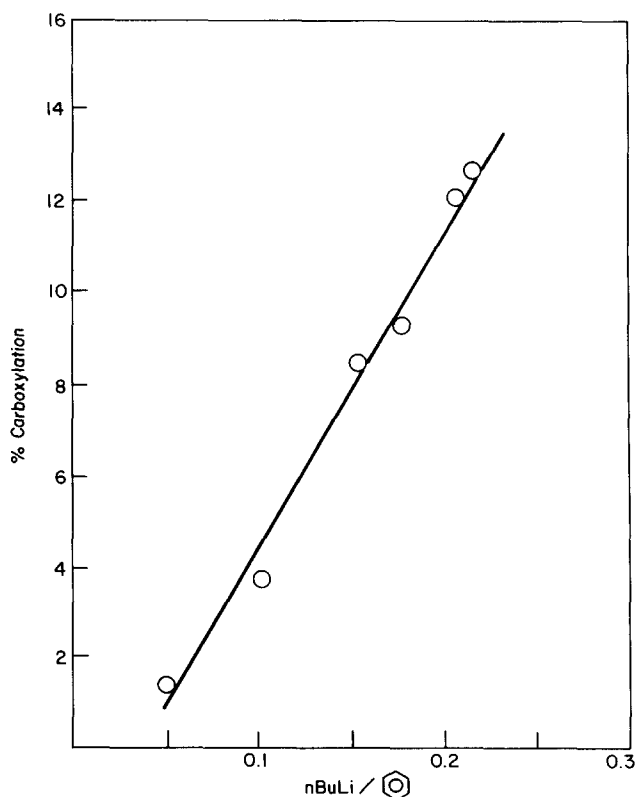
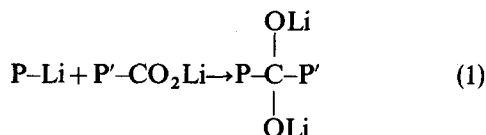


Figure 2 Per cent carboxylation (metallation) of poly(phenylene oxide) obtained versus amount of *n*-butyllithium used

on a different polymer molecule resulting in crosslinks¹² (equation (1)).



The effect of the heterogeneity on the carboxylation of PPO is revealed upon the fractionation of a PPO-CO₂H sample prepared at a nBuLi/Ar ratio of 0.75 (Figure 3). The sample contains fractions that differ in carboxylation levels by as much as 10%. The precipitation of fractions of increasing carboxylate functionality via the addition of water (nonsolvent) indicates uneven carboxylate sequence distribution on polymer molecules. Polymer molecules with uneven substitution are often less soluble than molecules with less functionality but a regular distribution of groups on the backbone¹³.

Attempts were made to increase the amount of metallation obtained in homogeneous solution by solvation of the metallated sites on the polymer backbone¹⁴. Metallations in the presence of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6-crown ether) and *N,N,N',N'*-tetramethylethylenediamine (complexing agents for lithium) did not reduce the interactions between metallated polymer backbones.

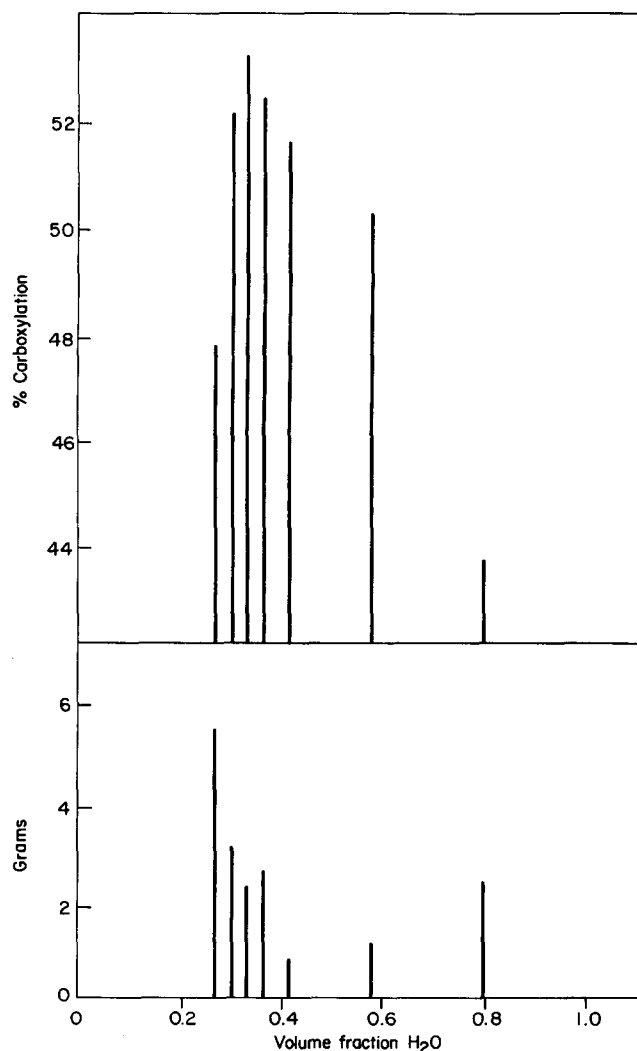


Figure 3 Fractionation of carboxylated poly(phenylene oxide) in a tetrahydrofuran/water solvent/nonsolvent system

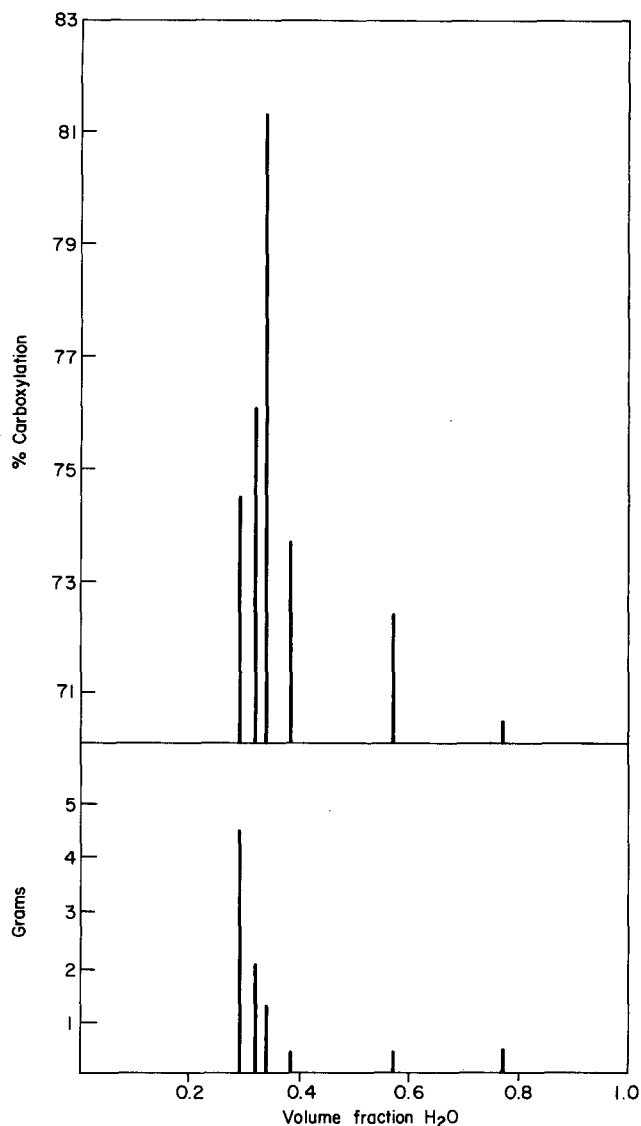


Figure 4 Fractionation of carboxylated polysulphone in a tetrahydrofuran/water solvent/nonsolvent system

Polysulphone (PS) was also successfully metallated and carboxylated by reaction with nBuLi and carbon dioxide. The PSF was found to precipitate at lower levels of metallation than PPO. Fractionation of PS-CO₂H sample prepared at a nBuLi/Ar ratio of 1.00 indicated uneven carboxylate substitution similar to that observed with PPO (Figure 4). Quantitative results of the metallation of PS, including location of metallation on the backbone, will be reported in a future publication.

The sodium salts of highly carboxylated (<40%) PPO and PS were completely water soluble up to 100°C. The effects of uneven carboxylate substitution resulting from the heterogeneous reaction conditions were observed in pressure cell solution studies at 121°C where fractional precipitation was observed. The maximum amount of carboxylate functionality that can be introduced on PPO while retaining a homogeneous reaction is 15%, not enough to obtain water solubility.

Hydrophilic comb-type graft terpolymers

To circumvent the metallation level limitation imposed by the onset of heterogeneity, homogeneous metallated PPO was functionalized with ester groups via the anionic oligomerization of methyl methacrylate from the lithium

sites. Hydrophilic and other groups could then be transesterified onto the MMA ester groups to yield comb type graft terpolymers with PPO main chains.

The reaction scheme for the attainment of the trigraft copolymers is illustrated in Figures 5 and 6. The first step consists of reacting PPO with *n*-butyllithium, followed by the capping of the metallated site with 1,1-diphenylethylene (DPE) and the oligomerization of methyl methacrylate. The second step is the transesterification of the MMA graft with hydrophilic oligomeric methoxy initiated polyethylene glycol.

The PPO-MMA graft copolymers were made via the method of Chalk and Hoogboom^{8,9} using a *n*BuLi/Ar ratio of 0.22 to maintain a homogeneous system at a maximum degree of metallation. 1,1-Diphenylethylene was then reacted with the metallated sites to prevent nucleophilic attack on the ester carbonyls of the methacrylate monomer¹⁵. Methyl methacrylate was then added to give an average chain length of five units. The ¹H n.m.r. spectra of the PPO starting material and the PPO-MMA graft copolymer are illustrated in Figure 7.

Owing to the random nature of the metallation and grafting reaction, the product was fractionated in a tetrahydrofuran/water solvent/nonsolvent system. The uniformity of composition (n.m.r. analysis) is illustrated by the fractionation profile in Figure 8. Relatively even DPE substitution (metallation) is observed among the fractions; however, the MMA chain length varies from 0 in fraction 1 to approximately 9 in fraction 7. To obtain a more consistent product for subsequent grafting, only the middle PPO-MMA fraction (broken lines in Figure 8) was selected for the transesterification study. This middle fraction contained polymer molecules of relatively consistent DPE substitution with MMA chain lengths of

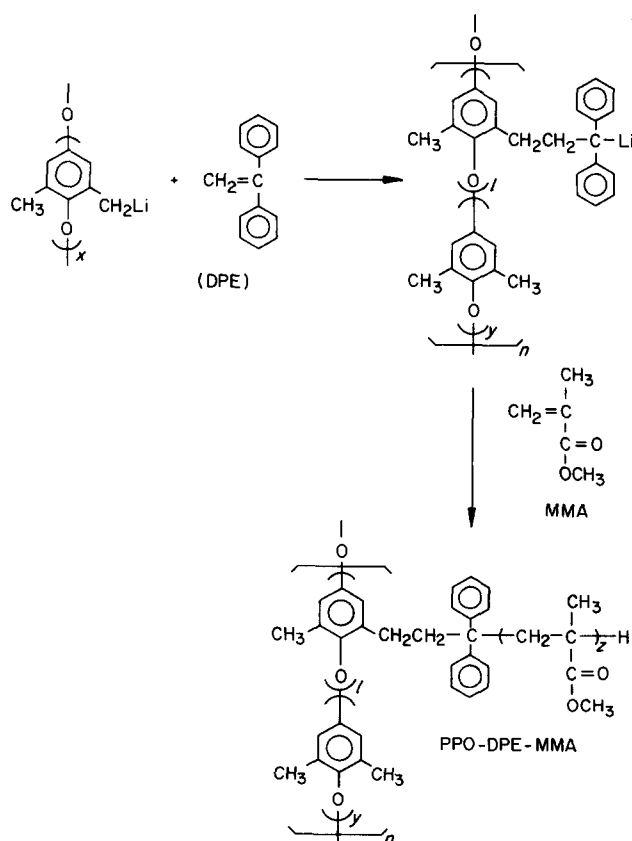


Figure 5 Synthesis of PPO-MMA graft copolymer

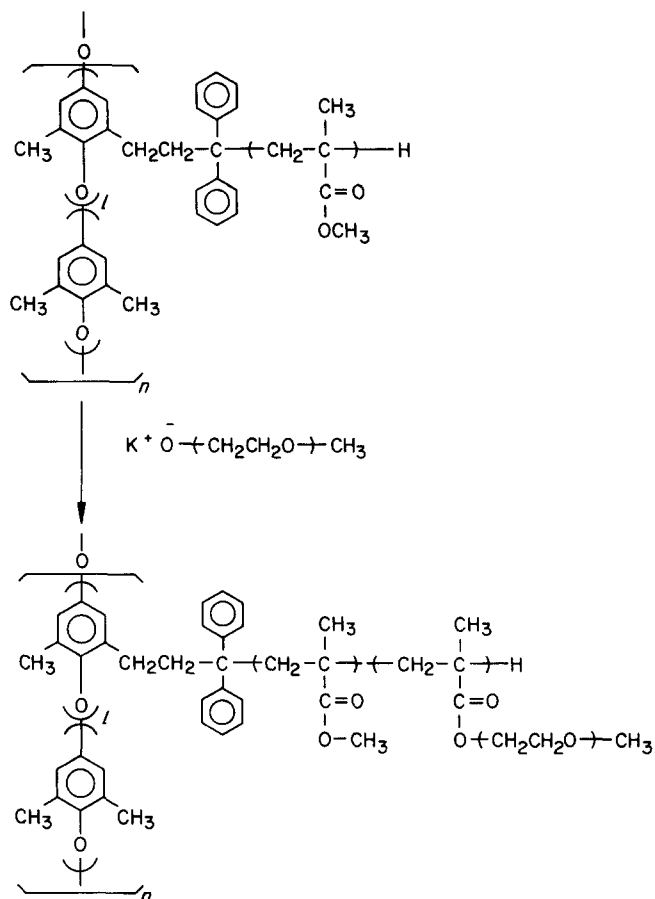


Figure 6 Synthesis of PPO-MMA-MPEG graft terpolymer

approximately 1–8 units. The results of the purification procedure on several different batches of crude PPO-MMA are illustrated in Table 1. The products are fractionated with respect to average MMA sidechain length; the average sidechain frequency is not as important. The synthesis and fractionation procedure can be used to obtain constant composition graft copolymers (Table 1, reactions 1–3) or to obtain products with different sidechain frequencies (different levels of metallation) while retaining equivalent average sidechain lengths (Table 1, reactions 4 and 5).

The procedure for the transesterification of the methoxy polyethylene glycol (MPEG) is diagrammed in Figure 6. Reaction conditions were based on previous studies by Twaik *et al.*³ and Thierry and Skoulios⁴; both reported the transesterification of polyethylene glycol to high molecular weight poly(methyl methacrylate). Twaik's method consisted of converting one half of the hydroxyls of difunctional polyethylene glycol to the potassium alkoxide and then reacting the glycol anions with PMMA in toluene. Thierry and Skoulios reacted monofunctional poly(ethylene oxide)-potassium alkoxide polymers with PMMA in toluene under vacuum line conditions. Both reported near quantitative transesterification, with Thierry and Skoulios reporting a more homogeneous product than that of Twaik.

To avoid potential crosslinking reactions, mono-hydroxy methoxypoly(ethylene glycol) (MPEG) was used. The hydroxyls were converted to the alkoxide with potassium naphthalenide and reacted with the purified PPO-MMA in toluene. Insoluble crosslinked products were obtained despite the use of MPEG as the esterifying

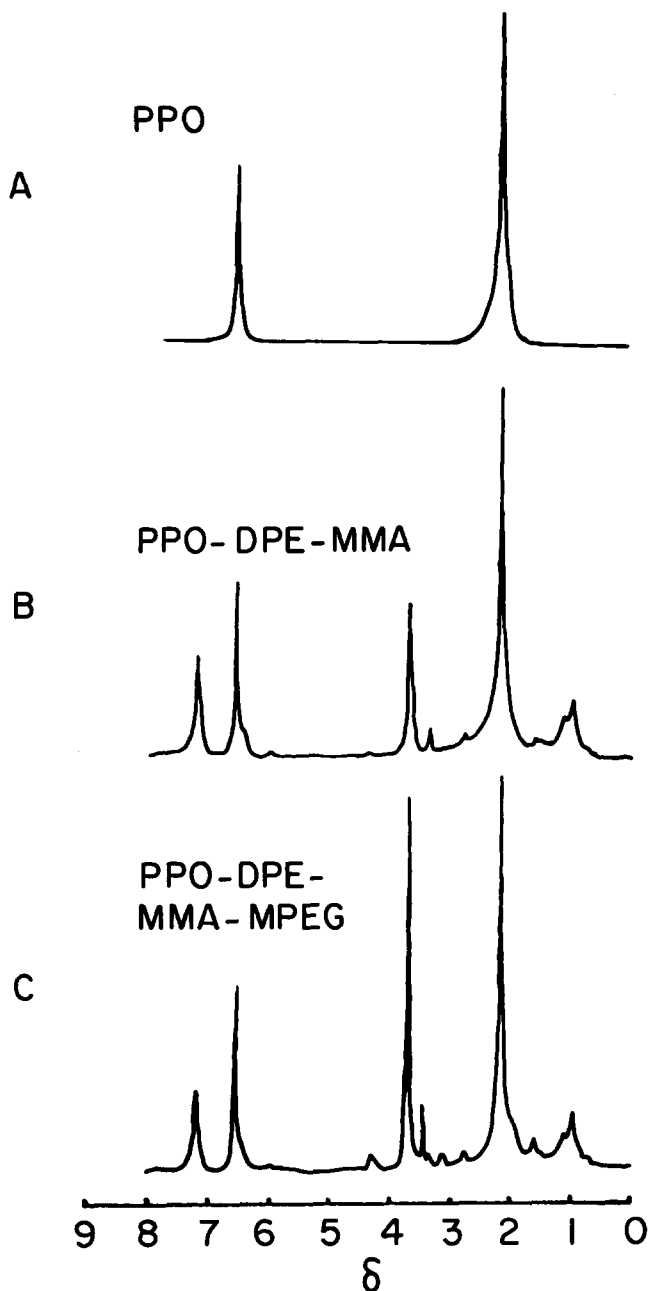


Figure 7 ^1H n.m.r. spectra of: (A) poly(phenylene oxide) starting material; (B) PPO-MMA graft copolymer; (C) PPO-MMA-MPEG graft terpolymer

agent. The major difference between the work of previous researchers and the present study could be the effect of PMMA endgroups. The previous studies used high molecular weight PMMA, where endgroup effects are insignificant. In this work, PPO-MMA utilized in the transesterification reaction contained MMA chains with an average of four units. Endgroup effects are very important with such short chains. A mechanism to account for the crosslinking is diagrammed in Figure 9; it involves abstraction of the terminal hydrogen of the MMA chain by the potassium alkoxide of MPEG. While the $\text{p}K_a$ values for the terminal hydrogen and the alkoxide do not favour the abstraction¹⁶, an equilibrium exists. Polyethylene glycols are known to form crown ether type complexes with alkali metals¹⁷. Complex formation would increase the basicity of the alkoxide¹⁸, further favouring abstraction of the terminal hydrogen. The end group anion could attack the carbonyl of an ester

group on another polymer molecule, forming a crosslink site and eliminating a methoxide anion. The reactions would be favoured by the temperature of the system (110°C)¹⁹.

To avoid the side reactions, the concentration of the alkoxide was reduced in the reaction by converting only part of the MPEG hydroxyls to alkoxides. To avoid polymer-polymer reactions the transesterification was run in more dilute solution with the PPO-MMA added slowly to the alkoxide solution. The results from the second set of reactions are given in Table 2. Transesterification was achieved in all of the reactions without crosslinking. The n.m.r. spectra of the PPO-MMA-MPEG terpolymer and precursors are illustrated in Figure 7. In reaction 12 (Table 2), the low yield is a result of loss of part of the product during workup in methanol. N.m.r. analysis of the methanol soluble fractions from all the reactions revealed only unreacted MPEG, except for those in reaction 12, which contained a small amount of the terpolymer graft. Attempts to separate the methanol soluble PPO-MMA-MPEG from the unreacted MPEG were unsuccessful.

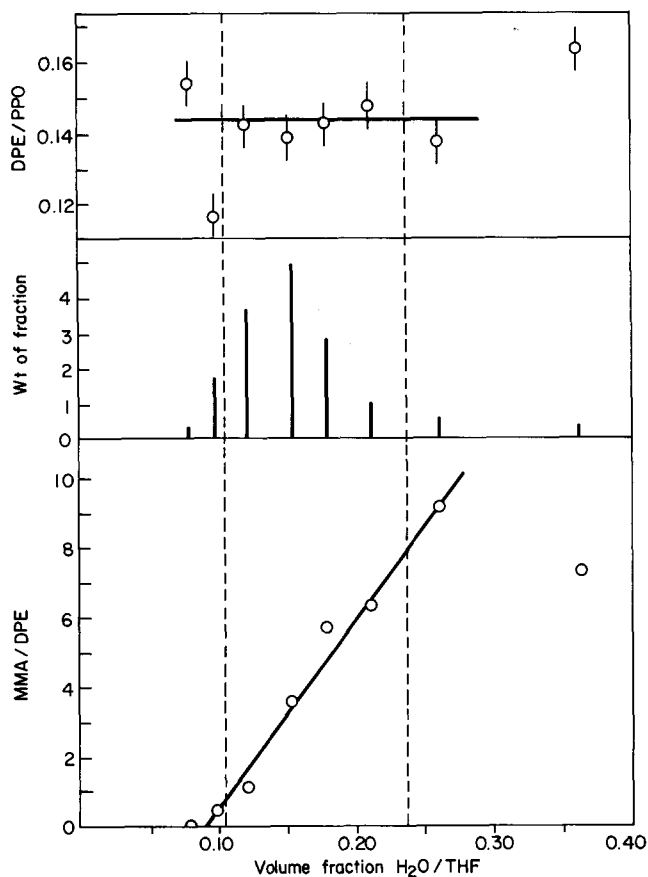


Figure 8 Fractionation of PPO-MMA in a tetrahydrofuran/water solvent/nonsolvent system

Table 1 Fractionation of PPO-MMA

Reaction	DPE/PPO ^a	MMA/DPE ^b	Yield (g)
1	0.13	3.9	12.7
2	0.13	3.4	13.1
4	0.12	4.5	11.0
3	0.15	4.5	13.3
5	0.10	4.3	12.4

^a Average side-chain frequency

^b Average side-chain length

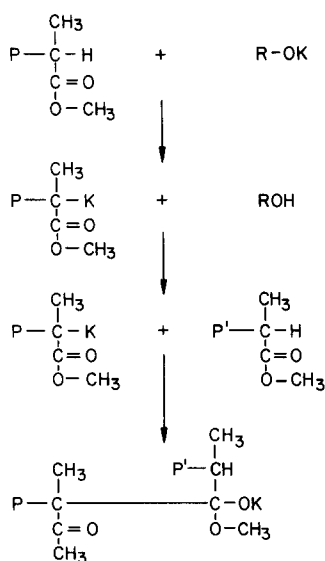


Figure 9 Mechanism for the crosslinking of PPO-MMA during transesterification

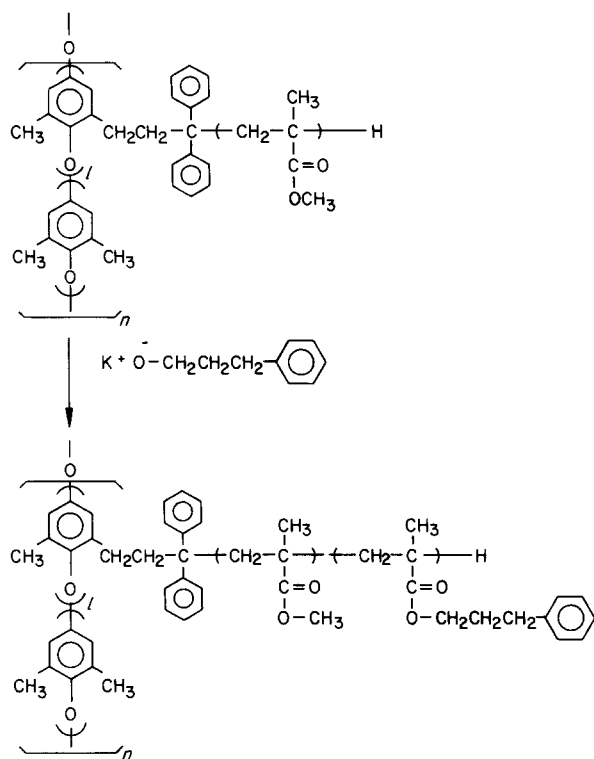


Figure 10 Transesterification of 3-phenyl-1-propanol on PPO-MMA

The PPO-MMA intermediate graft was also reacted with other hydroxy functional reagents. The transesterification of PPO-MMA with 3-phenyl-1-propanol is diagrammed in Figure 10. 3-Phenyl-1-propanol was chosen because its potassium alkoxide is soluble in the reaction solvent (toluene) and its aromatic protons are suitable for n.m.r. analysis.

The effect of 18-crown-6-crown ether on the transesterification of 3-phenyl-1-propanol (3P1P) with PPO-MMA was studied under the same conditions as in the transesterification with MPEG. The results (Table 3) are compared with reaction 10 from Table 2. Without the crown ether, more 3P1P is transesterified than MPEG due to less steric hindrance for the smaller 3P1P molecule. In addition, the presence of the crown ether significantly

Table 2 Transesterification of MPEG on PPO-MMA

Reaction	K/R-OH ^a	K/DPE	Found R-OH/DPE ^b	%Yield
9	0.04	0.23	0.30	86
10	0.09	0.50	0.58	89
11	0.27	1.24	0.84	88
12	0.42	2.27	0.24	65

^aR-OH = methoxypolyethylene glycol

R-OH/MMA ester = 1

^bDPE = MMA chain

Table 3 Transesterification of 3P1P on PPO-MMA

Reaction	K/R-OH ^a	K/DPE	Found R-OH/DPE ^a	CE/K ^b
10	0.09	0.5	0.58	—
13	0.09	0.5	0.83	0
14	0.09	0.5	1.12	1

^aReaction 10, R-OH = methoxypolyethylene glycol; reactions 13 and 14, R-OH = 3-phenyl-1-propanol

^bCE = 18-crown-6-crown ether, R-OH/MMA ester = 1

increases the amount of 3P1P transesterified (reaction 14, Table 3). The complexation of the potassium cation by the crown ether increases the nucleophilic strength of the alkoxide resulting in higher reaction yields¹⁶. In both reactions, more 3P1P is transesterified than was originally converted to alkoxide. The reaction is being driven toward completion by the removal of methanol.

CONCLUSIONS

Poly(phenylene oxide) and polysulphone can be made water-soluble by carboxylation. The synthesis is complicated by aggregation of metallated sites, causing polymer precipitation at high metallation levels. Fractionation studies of polymers carboxylated under heterogeneous conditions indicate uneven functionality distribution.

Methyl methacrylate can be anionically polymerized from metallated sites on a poly(phenylene oxide) backbone to give an ester-functional polymer, which can be transesterified with hydroxyl-functional reagents to give comb-type graft terpolymers. The use of methoxy-poly(ethylene glycol) oligomers as the hydroxyl-functional reagent results in a PPO backbone modified with nonionic hydrophiles. The two-step procedure yields well-defined trigraft terpolymers if fractionation is employed to obtain more homogeneous products and dilution conditions are employed to avoid crosslinking reactions. The amount of hydroxyl-functional reagent transesterified increased when a smaller reagent was used or a crown ether was present in the reaction, due to steric effects and increased alkoxide reactivity resulting from crown ether complexation of the potassium cation.

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