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Crown Ethers and Phase Transfer Catalysis in Polymer Chemistry

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Abstract: This paper is the first half of a two part review on the applications of crown ethers, cryptands, glymes and various onium ion salts to polymer chemistry. Part 1 surveys the use of these phase transfer catalysts (PTC's) in the synthesis and modification of macromolecules. Applications to ring-opening and vinyl polymerizations generally have involved solubilization and activation by PTC's of organic and inorganic salts which serve as anionic initiators. Change in the polymerization rates, polymer yields and product microstructure often resulted from association of the PTC with the active chain end.

Polymer modification and functionalization reactions have been enhanced by the use of PTC's. Macromolecular substrates have included both soluble and insoluble polymers, although the most popular have been the readily-available Merrifield resins. Generally these two-phase reactions have involved polymer solutions interacting with insoluble reagents or insoluble polymers reacting with the reagent solution. Some of the groups incorporated have been thiols, nitriles, carboxylic acids, esters, and crown ether analogs themselves. Most of this work has aimed at synthesis of polymer derivatives which can serve as chelating agents, catalysts and reagents in subsequent reactions. In almost all cases described, phase transfer catalysis offers definite advantages in selectivity and yield over conventional methods. The outline below gives the general subject areas of both Part 1 and Part 2; the latter will be published shortly.

PART I

- I. Introduction
- II. Polymer Synthesis via Phase Transfer Catalysis (PTC)
 - A. Ring-opening and Vinyl Polymerizations
 - B. Condensation Polymerizations
- III. Polymer Modification and Functionalization via PTC

PART II

- IV. Polymers Containing Pendant PTC Groups; Triphase Catalysis (TPC)
 - A. Crown Ethers and Cryptands
 - B. Onium Ions
 - C. Oligooxyethylenes (Glymes)
 - D. Miscellaneous Groups
- V. Polyoxethylene as a PTC
- VI. Polymers Containing Backbone Crown Ethers and Cryptands
- VII. Related Polymers and Potential Developments
- VIII. Summary and Conclusions

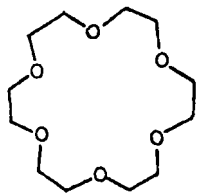
I. INTRODUCTION

The two parts of this review are intended to provide a reasonably comprehensive coverage of a small part of a field which has been enjoying explosive growth over the last ten years. In general this field includes applications of phase transfer catalysts (PTC's) to synthetic organic chemistry. Of course, other areas investigated include, for example, synthesis of new PTC's; elucidation of fundamentals of metal complexation and phase transfer processes; and comparison of synthetic and natural membrane transport agents. Some of these and other areas of present and potential interest will be described in appropriate sections in the body of the text.

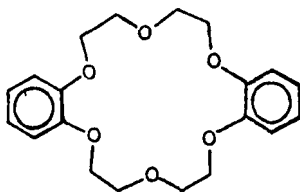
The generally accepted usage of the term "phase transfer catalysis" implies transport of an organic or inorganic salt from a solid or aqueous phase into an organic liquid phase where reaction with an organic-soluble substrate occurs. Often, the reaction could also take place in single-phase polar solvents or solvent mixtures but with less facility or much reduced yields. The acti-

vity of the anionic residue (generally in addition or substitution reactions) is enhanced in the nonpolar organic environment. The term "naked anion" describes the reduced or absent solvent sphere around the anion under PTC conditions, a situation which greatly affects reactivity and selectivity. While the use of the designation "phase transfer catalyst" may not be completely accurate since the PTC's are generally not involved in the actual reaction sequence it is nonetheless descriptively appropriate.

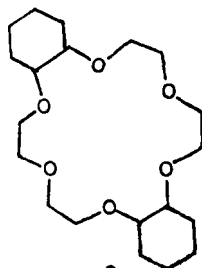
There are two basic types of PTC's including crown ethers and analogs on the one hand, and onium ion salts on the other. The former include compounds such as 18-crown-6 1, dibenzo-18-crown-6 2, dicyclohexano-18-crown-6 3; cryptands such as the [2.2.2] compound 4; and terminally capped and uncapped oligo-oxyethylenes 5. These species function by surrounding a metal cation (usually K^+ or Na^+) with a number of inward-facing oxygen or nitrogen electron lone pairs while at the same time providing an outer hydrocarbon coating which enhances solubility in a wide range of organic solvents. Furthermore, tight complexation of the cation by the chelating agents promotes ion separation and enhanced anion activity.



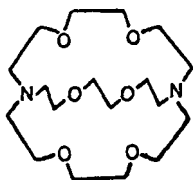
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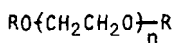
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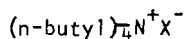
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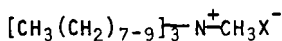
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The onium ion PTC's include the quaternary ammonium salts 6 and 7 (Adogen [®] 464) as well as a wide variety of phosphonium salts 8. These salts undergo ion exchange with the reagent salt in the aqueous phase or at the solid phase interface. Organic solubility results from medium to long alkyl groups on the onium cation, while the inherent nature of newly formed salts insures the ion separation necessary for increased anion activity.

A great many review articles and books have appeared recently on the synthesis of various types of PTC's ^{1,2} and their application in organic synthesis. ^{3,4} Nomenclature and complexation constants have been adequately covered in these and other ⁵ references and will not be mentioned here. The nature of the activity of these compounds and the advantages of their use in synthesis made it inevitable that they be applied to polymeric systems. In our previous short survey of the use of crown ethers in polymer chemistry ⁶, we gave representative examples of several important areas. The present review is intended to be as comprehensive as possible and includes work published through the middle of 1980. The breadth of this field, however, and the availability of several review articles on specific aspects of the field requires that not all subjects or references be covered in complete detail. Interest in these areas may be pursued through references to the original articles or appropriate reviews which are given in the individual sections.

Subject areas included here cover mainly phase transfer applications. Obvious uses include PTC for polymer synthesis and modification as well as applying polymer-pendant PTC's to organic synthesis in general. Work is also described which deals with linear polymers (eg., polyoxyethylene) as PTC's and with polymers containing crown ethers and cryptands in the backbone for use in cation chromatography and separation. Additionally, some recent developments in crown ether-related areas which have potential for polymer applications are also included. Finally, some general observations and conclusions are given dealing with the unique properties arising

from the combination of PTC's with polymers. Hopefully this review will provide sufficient background for impetus and development of new applications of this increasingly important area.

II. POLYMER SYNTHESIS WITH PHASE TRANSFER CATALYSTS (PTC's)

A. Ring-opening and Vinyl Polymerization

In our previous review,⁶ we described several applications of crown ethers and cryptands in addition, ring-opening and condensation polymerizations. For chain growth systems, increased and modified anion activity was related to cation complexation by the macrocycles. Solubilization of the polar salts in non-polar solvents and enhanced ion separation were apparently the controlling factors. Examples of ring-opening polymerizations described⁶ included β -propiolactone with sodium acetate and 2, and 2-pyrrolidone with 4 and the potassium salt of the monomer. Butadiene homopolymerization and copolymerization with styrene were carried out in hexane with n-butyl sodium and 3 to give higher molecular weight products with higher conversion than without 3.

A more complete examination of the β -propiolactone polymerization has recently appeared.⁷ Dichloromethane was used as solvent with an initiator system of dibenzo-18-crown-6 (2) plus potassium acetate. Slomkowski and Penczek found that increasing the crown-to-salt ratio led to a linear increase in the rate of polymerization up to a maximum for a 1:1 ratio indicating essential complete complexation of the potassium acetate. A linear dependence of \bar{M}_n with conversion led to the conclusion that no termination or transfer processes were involved in this polymerization; ie, this is a "living" anionic system. Determination of dissociation constants and extensive kinetic analysis indicated that the propagating carboxylate anion and the crown-complexed potassium form a loose ion pair in CH_2Cl_2 . The individual rate constant for propagation of the free anion was always greater than that of the ion pair, varying from a ratio of 150 at 35° to 5.6 at -20°. This work

clearly indicates the activating influence of the crown ether in promoting loose and free ion pairs of the propagating polymer anion.

In our earlier review we failed to include several pioneering papers on the use of crown ethers and cryptands to initiate anionic alkene polymerizations via complexation with alkalai metals and alkalai salts. In the first of these, for example, styrene was polymerized quantitatively in benzene or THF using metallic lithium and the [2.1.1] cryptand analogous to 4⁸. The polymerization was completed in seconds to give \bar{M}_w in the millions. Similarly rapid reaction of methyl methacrylate in THF with lithium, sodium or potassium-naphthalene and an appropriate cryptand gave a highly syndiotactic polymer again with \bar{M}_n in the millions.⁸ Cryptates (cryptand complexes) were also observed to be exceptionally active initiators for the polymerization of isoprene, propylene sulfide and ethylene oxide.⁸ A continuation of this work reported on the ready formation of complexes of alkalai sodium-through-cesium metals which were soluble in relatively poor solvents (for these species) such as benzene, toluene, THF, dioxane and tetrahydropyran.⁹ These complexes readily formed the dianions of α -methylstyrene and 1,1-diphenylethylene which initiated the generally instantaneous polymerizations of butadiene, isoprene, styrene, methyl methacrylate and 2-vinylpyridine. Even normally inactive alkalai salts were found to be capable of initiating polymerizations when complexed with cryptands.¹⁰ In benzene, for example, the 4 cryptates of KOH and sodium t-amylate respectively polymerized hexamethylcyclotrisiloxane and styrene in good yields. Propylene sulfide and isobutylene sulfide were initiated with the cryptates of KCNS and potassium t-butoxide, respectively.¹⁰ Detailed analysis of the kinetics of the cryptate-promoted polymerizations of propylene sulfide¹¹ and ethylene oxide¹² have also been reported by Boileau and coworkers.

Two more recent reports have appeared on the effects of crown ethers on anionic polymerizations. The first of these¹³ extends

earlier work on the polyaddition of methyl methacrylate initiated with lithium salts in the presence of various cryptands and crown ethers (see references in ¹³). The present paper employed other alkali metals directly as initiators. In the presence of dicyclohexano-18-crown-6 (3) the four metals Na, K, Rb and Cs all readily dissolved in nonpolar solvents such as benzene and toluene. ESR evidence for the potassium solutions at -70° indicated that dissolution actually involved formation of the crown-complexed metal cation and the radical anion of benzene or toluene. Polymerizations were carried out at -78° or from 0° to 25° and generally gave complete conversion in less than a minute. Relatively broad molecular weight distributions were obtained with molecular weights in the range $3-8 \times 10^5$ daltons. NMR analysis of the polymer microstructures indicated predominantly syndiotactic products with essentially Bernoullian statistics. Slight increases in the syndiotactic content with the metal used were observed with the order being $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+$. Yields and tacticities were comparable to those obtained with lithium in dioxane and sodium in benzene plus the [2.2.2] cryptand.

A second paper from the same research group¹⁴ described the use of the same four metals for polymerization of butadiene and isoprene. Both the crown ether 3 and the cryptand 4 were employed with benzene and THF as solvents to give homogenous initiator solutions. Polymerizations were carried out at 10° with benzene and -78° with THF. Reactions were complete in one minute with yields of 99-100%. With isoprene in benzene plus 3, small differences in the polymer microstructure were observed with the various metals. The 1,4-, 3,4- and 1,2-contents went from 21:60:19, respectively, for potassium to 42:41:17 for cesium. Much less structural variation was observed in THF although the 1,4-residues decreased significantly with the contents being 12-18:46-50:30-40, respectively.

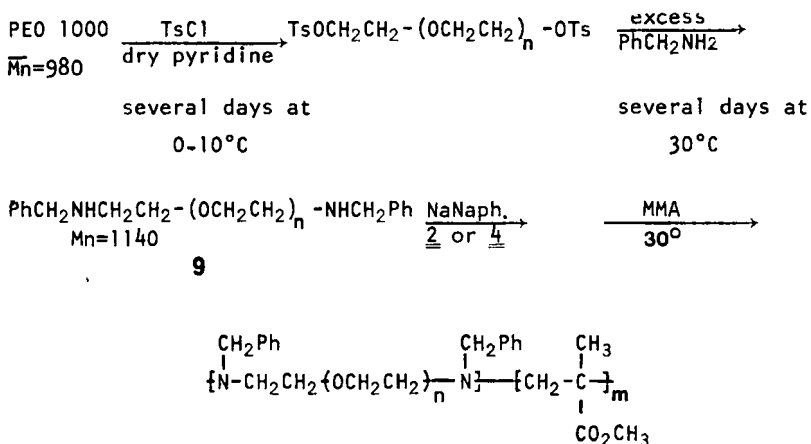
For butadiene polymerization in benzene with 3, the 1,2-content increased in the order $\text{Cs} < \text{Rb} < \text{K}$. When the cryptand was

employed, however, all four metals gave essentially the same polymer with a 72-74% 1,2-structure in benzene and 79-86% 1,2-content in THF. While the use of the cryptand rather than the crown ether increased the 1,2-content for all the metals used, the change for potassium was small in both benzene and THF. This plus the leveling effect observed for all four cryptates may be directly attributed to the thermodynamics of metal complexation. The crown ether forms a stronger complex with the potassium cation (which fits exceptionally well into the crown cavity) than with the other larger or smaller alkali ions. The cryptand, however, forms relatively tight complexes with all four cations mainly because of its bicyclic structure and additional chelating groups.

The butadiene results may be compared to an earlier report¹⁵ in which polymerizations were carried out in hexane, generally at 30°C, with n-butyl sodium and dicyclohexano-18-crown-6 (3) as the cocatalysts. Under these conditions but without the crown ether, butadiene gave a low molecular weight polymer in low conversion. With crown ether present, however, high conversion and high molecular weight were obtained: eg, with inherent viscosities of 1.7-5.2 dl/g. Conversion was somewhat related to the ratio of initiator to crown ether and increased to 95% at higher crown ratios. These changes were attributed to a decrease in the termination reaction brought about through stabilization of the chain end by the crown ether. Of additional importance was a slight increase (from 68-80%) of the vinyl content of the polymer with a decreasing sodium-to-crown ether ratio. The 1,2-percentages were comparable to those obtained in benzene under similar conditions with K, Rb and Cs.

An interesting application of PTC to the synthesis of a block copolymer was based on an initial attempt by Suzuki and coworkers to synthesise block copolymers of oxyethylene and methyl methacrylate.¹⁶ Using the disodium salt of polyoxyethylene (POE) to initiate the anionic polymerization of the vinyl monomer led to products with broad and multimodal molecular weight distributions. Transesterification of the POE terminal anion with the methyl ester

was apparently partially responsible. A more active POE derivative was then synthesized and combined with crown ether and cryptand catalysis.¹⁷ Thus, the POE 1000 ($M_n=980$) was converted to the corresponding diamine (9):



The secondary amine groups were then converted to the anions with sodium naphthalene in tetrahydrofuran. Either dibenzo-18-crown-6 (2) or the cryptand 4 was added followed by the methyl methacrylate and the polymerization then carried out at 30°. Product molecular weights and molecular weight distributions were determined with comparative GPC and ¹H NMR. Comparison of these values with those of a polymer prepared without a PTC indicated a slight increase in yield with the crown ether and a significant skewing of the MWD to higher values with the cryptand catalyst. The unusual behavior of the polymers in the GPC analysis and somewhat confusing results presented make it difficult to draw any firm conclusions on the effect of the PTC on the course of this reaction. Hopefully, the full paper will clarify these results.

B. Condensation Polymerizations

Several new polycondensations have appeared since the previous survey. A new synthetic route to polycarbonates described

by Soga and coworkers involves the reaction of α,ω -dibromides with potassium carbonate in various organic solvents carried out in the presence of several crown ethers.¹⁸ With *p*-xylylene dibromide (Figure 1, upper path) the effects of crown ether, solvent, temperature and time on polymer yield and molecular weight were all examined. Diglyme as solvent with 18-crown-6 gave the best yields (50-60%) for high molecular weight products ($\sim 12,000$ daltons). Polyoxyethylenes of $\overline{DP} = 4$ and 25 were not efficient catalysts. The rate of polymerization increased with temperature to a maximum at $100-120^\circ$ and then decreased slightly. At 105° the molecular weight gradually increased with time to an apparently asymptotic value at 48 hours. Surprisingly, polymer prepared at 160° gave evidence of polyether incorporation, presumably through crown ether ring-opening and incorporation into the backbone. The ratio of catalyst to K_2CO_3 was found to be important with a value of 1:10 giving the best yield and molecular weight values.

Similar reaction conditions were applied to a series of α,ω -dibromoalkanes (Figure 1, lower path). For the ethane and propane derivatives, only cyclic carbonates with 5- and 6- membered rings, respectively, were obtained. With several higher alkanes, reasonable yields of high molecular weight ($> 20,000$ daltons) products were obtained. In general, this method provides an

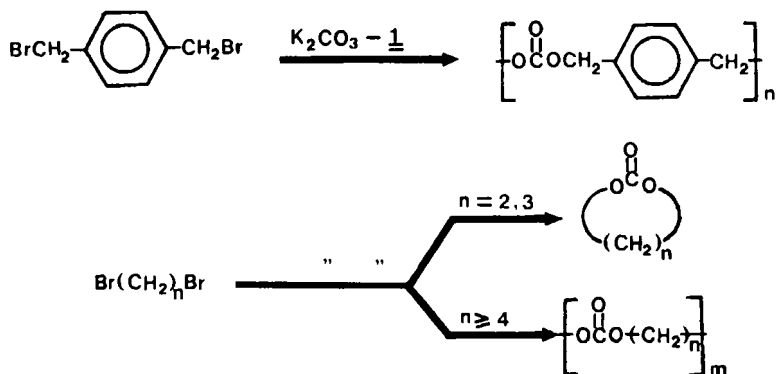


FIG. 1.

excellent alternative to previously available techniques, and complements the use of CO_2 rather than K_2CO_3 as the carbonate source in the PTC synthesis of polycarbonates described earlier by Soga, et. al.,¹⁹

Soga's group has also reported a similar procedure for synthesis of a polythiocarbonate.²⁰ The polycondensation involved α - α' -dibromo-p-xylene with CS_2 and the dipotassium salt of 1,4-cyclohexanediol. The reactions were carried out neat or in dioxane, benzene, THF, DMF or acetone solvents with 18-crown-6 as the PTC. At temperatures above 0° , a copolymer was obtained (Figure 2) which resulted from direct attack of the alcoholate anion on the halide along with the desired intermediate formation and attack of the dithiocarbonate. At -78° , however, exclusive formation of the polydithiocarbonate (Figure 2) was observed when CS_2 was employed as solvent as well as reagent. Variation in reaction time and PTC content did not markedly affect polymer yield or molecular weight. Values of \bar{M}_n were found to be in the range 1300-2300 daltons. The use of PTC in this case might be best viewed as a means of obtaining oligomers and prepolymers.

Two virtually simultaneous reports have appeared on the use of PTC to synthesize polysulfide elastomers. Imai's group investigated the condensation of, for example, 1,4-dibromobutane with 1,6-hexanedithiol (Figure 3).²¹ While polymer was obtained without catalysts, the rate of reaction and inherent viscosities were significantly increased with PTC's like dibenzo-18-crown-6 and tetrabutylammonium chloride (6). The highest viscosities were

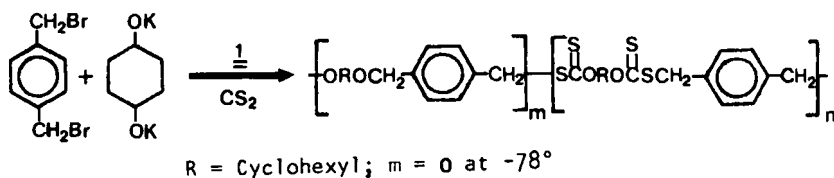


FIG. 2.

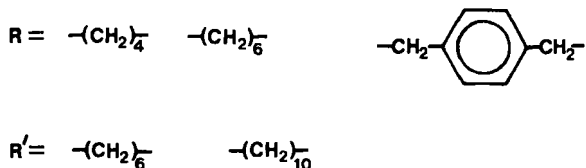
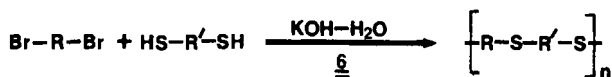


FIG. 3.

obtained at 80° and in the absence of solvent. Yields were essentially quantitative for this polymer and for the five related polysulfides described.

Petitt has used tetrabutylammonium hydroxide to enhance the rate and yield of the well-known polymer obtained from sodium polysulfide (sulfur dissolved in 10-15% aqueous sodium hydroxide) and 1,2-dichloroethane.^{22,23} With or without dichloromethane as solvent for the latter, the polymerization was complete in 5 minutes at reflux temperature with the catalyst, while 45 minutes was required in the absence of the PTC. Similar reaction with 2,3-dibromopropanol and 1,2-dibromostyrene required 12-15 minutes for complete reaction. As expected, reaction of chloroform with the sodium polysulfide (perhaps via the dichlorocarbene) occurred with dichloromethane as the solvent in 30-40 minutes. The yield of polymer was somewhat low and the chlorine content much less than that expected from the suggested reaction pathway. In any event, this procedure provides a convenient demonstration of the application of PTC to polycondensation experiments which may be readily incorporated into general organic and polymer laboratory courses.

In addition to polythioether synthesis, Imai and coworkers have applied PTC's to a number of other polycondensation systems (see reference in this collection). Our earlier survey described aromatic polyether formation via condensation of bis(4-chloro-3-

nitrophenyl)sulfone and 2,2-bis(4-hydroxyphenyl)propane (Figure 4, upper path). The use of crown ethers 2 and 3 allowed essentially quantitative conversion at much lower temperatures (27°) with a CH_2Cl_2 -KOH- H_2O mixture.²⁴ This report also contained what is probably the first application of linear polyoxyethylene as a PTC in polymer synthesis, a subject discussed more thoroughly in a later section of this review.

An earlier paper from this group was concerned with the synthesis of an aromatic polysulfonate from a disulfonyl chloride and bis-phenol A (Figure 4, lower path).²⁵ Interfacial condensation in the absence of a PTC led to a limiting $[\eta]$ of 0.2 dl/g. A series of crown ether PTC's including 1 - 3 and various others gave $[\eta]$ values greater than 0.8 dl/g. With all of the PTC's, KOH gave better results than NaOH. With KOH and 3, for example, polymer with $[\eta]$ of 1.48 dl/g was obtained in quantitative yield after 3 hours at 20°C.

The above examples along with others in this symposium collection and those appearing continually in the literature indicate the potential that PTC offers in the synthesis of chain- and step-growth polymers. Modification of vinyl and diene polymer microstructure on the one hand and enhancement of the rate and/or yield of ring-opening polymerizations and polycondensations on the other are some of the more obvious advantages. The example included here

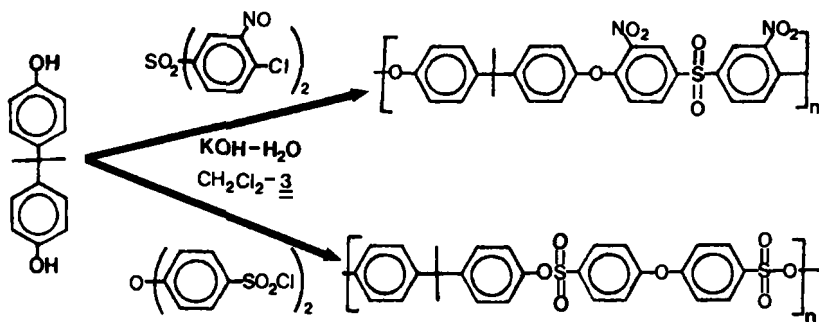


FIG. 4.

of the synthesis of a block copolymer using PTC indicates some further areas of application among many which should be explored; eg, anionic random and graft copolymerizations. This area is one which should enjoy enormous growth over the next few years.

III. POLYMER MODIFICATION AND FUNCTIONALIZATION

The second main area of PTC applications to polymers is one that has recently enjoyed extensive investigation. It involves the chemical modification of functional polymers using two- and three-phase systems. The former may involve liquid-liquid or liquid-solid reactions while the latter generally involves two liquid phases interacting with an insoluble polymer. This area was not covered in our earlier survey although several reports had appeared in 1976 and 1977.

Roovers published what seems to be the earliest report on the use of PTC in polymer modifications in 1976.²⁶ The substrate polymer was a soluble, chloromethylated polystyrene with an \bar{M}_n of 143,000 daltons. Reactions were generally carried in 50:50 benzene-acetonitrile at 75° with either dicyclohexano-18-crown-6 (3) or dibenzo-18-crown-6 (2) as the PTC. The former was about twice as efficient as the latter under these conditions. The nucleophiles employed included a variety of potassium carboxylates which formed the corresponding bound esters (Figure 5). The following acid anions were used (with yields or % incorporation in parentheses): acetate (100%); benzoate (100%); trans-cinnamate (87%); and 1-phenylpropionate (100%). The latter served as a model system for reaction of mono-carboxylate-terminated polystyrene ($\bar{M}_n = 3000$ daltons). Essentially complete conversion to the graft or comb-polymer was observed with this procedure.

The obvious potential for application of this method to the insoluble Merrifield resins was verified almost simultaneously with the above report.²⁷ Potassium salts of various t-butyloxy-carbonyl-(or Boc)-protected amino acids were reacted with the resins using 18-crown-6 as the PTC. For example, at 100°

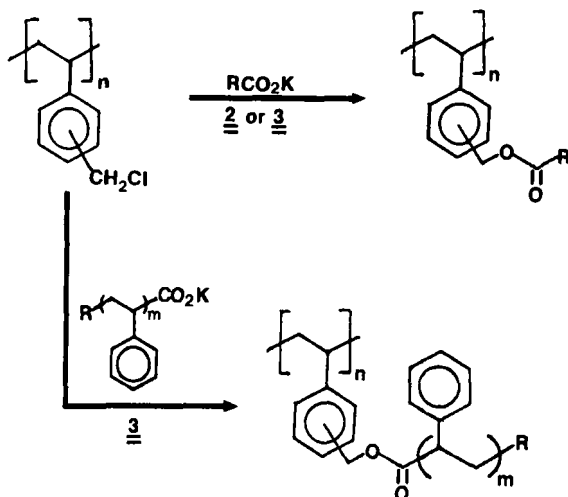


FIG. 5.

and with one equivalent of PTC essentially complete incorporation of Boc-leucine was observed in several solvent systems (Figure 6, upper path). At lower temperatures, however, only dimethylformamide (DMF) gave good results. At room temperature, excess catalyst and amino acid salt were required for complete conversion in 18 hours. With the latter conditions only five of the twelve amino acids examined gave >90% incorporation. At 50° with 1.2

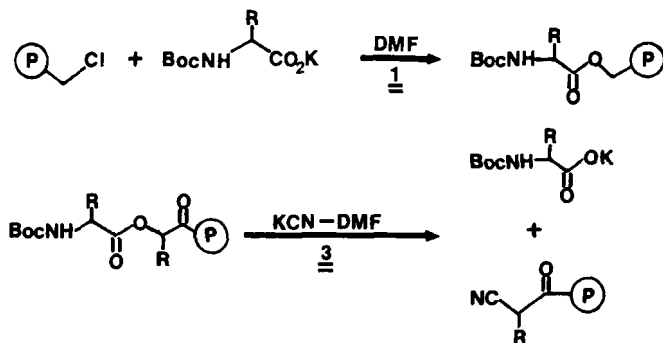


FIG. 6.

equivalents of salt and PTC, all twelve were incorporated at >89% in 18 hours. Although not reported, recemization under these relatively mild conditions should be very low. Thus, PTC offers an excellent alternative to other methods for the first step of the traditional solid-phase peptide synthesis.

In a related vein is a report on the mild cleavage of peptides from a different Merrifield support using PTC (Figure 6, lower path). The resin binding moiety was the phenacyl ester group ($R=H$) or its methyl analog ($R=CH_3$). While cleavage of the protected amino acid or peptide from this resin could be effected with other reagents, eg., hydrazine, side reactions such as cleavage of side-chain benzyl ester groups also took place. However, use of KCN with crown ether 3 and DMF, N-methylpyrrolidone or acetonitrile gave clean and high-yield removal of the peptide or amino acid derivative. For example, removal of a heptapeptide took place in 86-93% yield. It is somewhat surprising that to the best of our knowledge the use of PTC for solid-phase peptide synthesis and cleavage has not been further investigated.

Two other groups have been investing much effort in the exploration of PTC applications to polymer synthesis and modifications. Boileau in France and Fréchet in Canada along with their respective coworkers have each published several reports in recent years including one in this symposium collection. Again the readily available and well-characterized chloromethylated polystyrene provided the main substrate polymer for the modification work although Boileau's efforts have also involved reactions on epichlorohydrin polymers.

Polyepichlorohydrin and copolymer with ethylene oxide were modified by carbazole incorporation (Figure 7). With a tetrabutylammonium PTC (6) at 5 mole-% and a temperature of 60°, the highest conversions (31%) were obtained on both polymers using DMF as the solvent.²⁹ Other solvents gave less than 10% conversion. Increasing the catalyst concentration up to 100 mole-% gave only a modest increase in conversion (to 56%) while increasing the re-

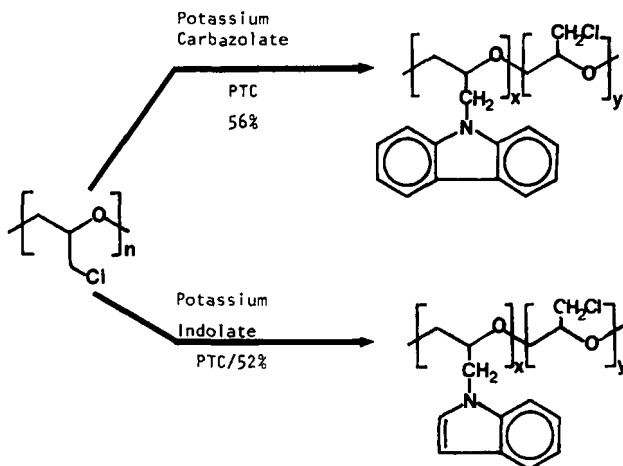


FIG. 7.

action time beyond 5 hours did not markedly effect the incorporation. Comparable degrees of substitution could be obtained with only 5 mole-% of either dicyclohexano-18-crown-6 (3) or the [2.2.2] cryptand 4 indicating a higher catalytic efficiency for these compounds. With a soluble chloromethylated polystyrene, however, essentially complete substitution by carbazole was observed even with the TBA catalyst. A commercial Merrifield resin gave similar results. 2,3-Dimethylindole and a variety of alkyl amines were reacted with the polyepichlorohydrin with poor results (<10% incorporation) for the latter and good incorporation (52%) for the former (Figure 7). With the soluble chloromethylated polystyrene, high conversions (>65%) were obtained with both alkyl and heterocyclic amines.

Several reactions on the soluble chloromethylated polystyrene were further explored subsequently by N'Guyen and Boileau.³⁰ The polymer (dissolved in DMF) was treated at 60° with 1.5 equivalents of the reactant in aqueous 50% NaOH. The PTC was tetrabutylammonium hydrogensulfate at 5 mole-% and reaction times varied from 0.75 to

3 hours. The following is a list of reactants incorporated along with the % substitution in parentheses: N,N-diethanolamine (75%); p-methoxybenzylalcohol (100%); 2,6-dimethylphenol(93%); 2-mercaptopyridine (82%); phthalimide (87%); phenylacetonitrile (82%); indene (70%); propionic acid (100%); sodium cyanide (95%) and sodium thiocyanate using the [2.2.2] cryptand (76%). The cyanide incorporation is noteworthy because Roovers reported no reaction of a similar polymer with KCN under comparable conditions. Molecular weights (\bar{M}_n) of the product polymers indicated no degradation. Indeed, for the 2,6-dimethylphenol and phenylacetonitrile derivatives the observed \bar{M}_n 's were greater than those calculated. This was attributed to some C-alkylation and dialkylation, an hypothesis which will hopefully be verified in the promised full paper.

Fréchet's work has been more extensive and has involved some important basic considerations. For example, one of his group's publications in this area dealt with reaction of a difunctional nucleophile, 1,4-butanedithiol, with a lightly-cross-linked chloromethylated polystyrene.³¹ In both the presence and absence of a PTC, a high degree of double coupling (ie., further cross-linking) with the dithiol was observed (up to 87%). Only when a large excess of dithiol and base were used (2.6:1.0) with respect to the chloromethyl concentration (0.15 relative ratio) was single coupling obtained in high degree (95%). This work (along with numerous related investigations of site-site interactions in cross-linked polymers) has important consequence to the use of polymers as protecting-groups and anchors for multifunctional compounds.

Three-phase catalysis has been applied to the generation of polymer-bound sulfonium ylids which were then used to form epoxides (Figure 8)³². The dimethyl or diethyl sulfonium intermediate was converted to the ylid and used in epoxide synthesis using DMSO as solvent. After two reaction cycles the polymeric reagent had lost all activity. However, when three-phase conditions were used with tetrabutylammonium salts as the PTC, no loss of activity was observed even after five repetitions. The ease of recovery

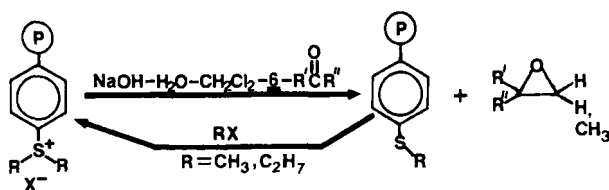


FIG. 8.

and lack of odor of these polymeric reagents coupled with the higher yields of products makes this an excellent system for these and related reactions.

A wide range of nucleophilic substitutions have been reported by Fréchet and coworkers on cross-linked polystyrene derivatives, with the chloromethylated compound being the most heavily investigated.³³ Some of the more valuable conversions are outlined in Figure 9. Solvents (or swelling agents) included *o*-dichlorobenzene, 1,2-dichloroethane, dichloromethane and benzene while the PTC's were quaternary ammonium salts 6 and 7. Conversions in most cases were greater than 95%. A three-phase system was also used to convert the chloromethyl groups to thiomethyl groups with excellent conversion, although an inert atmosphere was required to eliminate site-site disulfide formation.

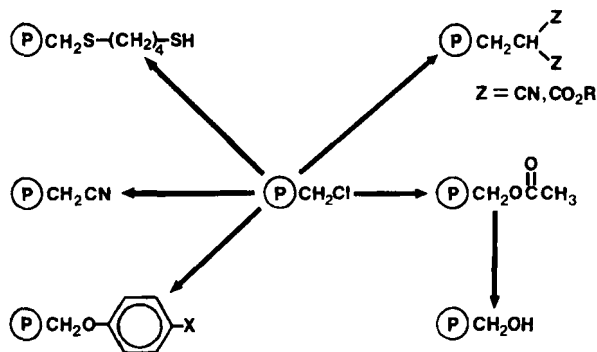


FIG. 9.

A number of additional modification reactions employing PTC's were also reported involving several insoluble polymeric aldehydes, thiols and phenols.³³ Cyanohydrins formed from the aldehyde groups were trapped as the acetate or p-nitro-benzyl ether. An interesting reversal of activity for three-phase systems employed the polymeric thiols and phenols as the nucleophiles. Reaction with various alkyl halides led to ethers and thio ethers in excellent yields.

A subsequent report of the conversion of chloromethylated polystyrene to dinitriles and diamines³⁴ was later complemented by an extensive investigation of similar compounds by another group.³⁵ Fréchet and his colleagues treated insoluble chloromethylated polystyrene with the anion of malonitrile under three-phase conditions to give the polymer-bound dinitrile in essentially complete conversion (Figure 10). When p-cyanomethylated polystyrene was used as the nucleophile with chloroacetonitrile under similar conditions, conversion to the isomeric dinitrile occurred in 88% yield. Both of these derivatives were quantitatively reduced to the corresponding diamines with LiAlH_4 .³⁴

Ricard and co-workers reported a slightly different procedure for incorporation of the 1,3-diaminopropane group (Figure 11, upper path). Acylation of the polystyrene with chloroacetyl chloride was followed by a three-phase reaction with malonitrile directly or after initial reduction of the ketone group to an alcohol. The former gave a much higher overall yield of the polymer-bound diaminoalcohol.³⁵

This report further described the incorporation of various diamines and diols into a 12% cross-linked Merrifield resin. Again

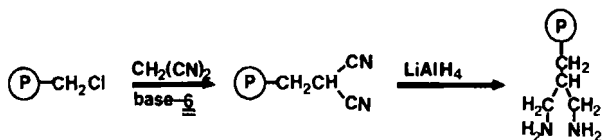


FIG. 10.

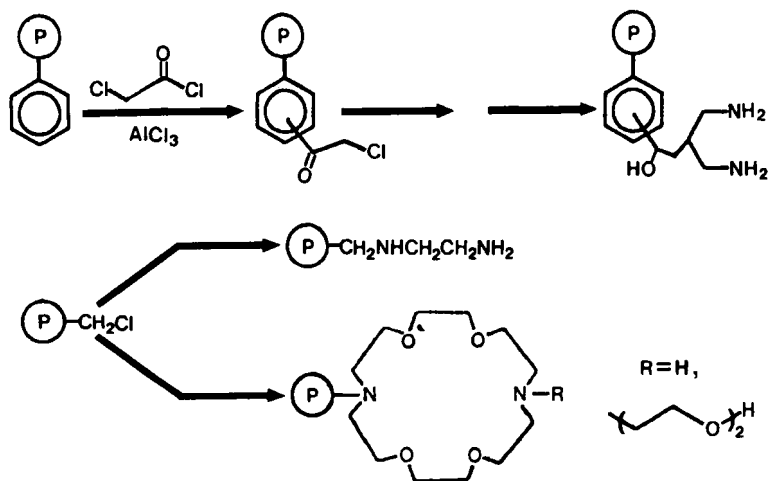


FIG. 11.

using a three-phase system, the chloromethyl groups were converted to various aminomethyl derivatives (Figure 11, middle path). Other diamines examined included 1,2-diaminobenzene and 1,8-diaminonaphthalene. Despite a large excess of diamines, the low yields and the probability of double-coupling indicate a need for more efficient reaction conditions for these modification procedures, perhaps through the use of PTC's other than the benzyl trimethylammonium salt employed here. Nonetheless, the two polymer-bound crown ether derivatives (Figure 11, lower path) did display activity as PTC's and transition metal chelates. This work is reportedly under further development.

An initial communication recently appeared³⁶ which portends further developments in polymer modification. Poly(vinyl chloride) was allowed to react in THF with solid potassium acetate and 18-crown-6 (1). The reaction was carried out at 46° for varying times and with a range of crown ether concentrations. Up to 7% chlorine replacement by acetoxy groups (measured by quantitative IR) was observed although the "labile" chlorine content of PVC is usually considered to be about 0.1%.³⁶ Although appar-

antly there was considerable substitution of the normal secondary chlorines under these conditions, high degrees of substitution were limited by degradation of the PVC with very long reaction times (>70 hours). The degradation involved formation of highly colored material presumably resulting from dehydrohalogenation or loss of acetic acid.

It is clear from these many examples that the application of PTC's to polymer modification and functionalization reactions has tremendous proven and potential value. With the proper choice of conditions, many mono- and difunctional compounds react with relatively clean incorporation, although double coupling (resulting in site-site cross-linking) limits application of the latter to insoluble resins. The ease of reaction and work-up, the high conversions, the apparent generality of these two-phase and three-phase modifications should make this the method of choice for many such reactions.

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