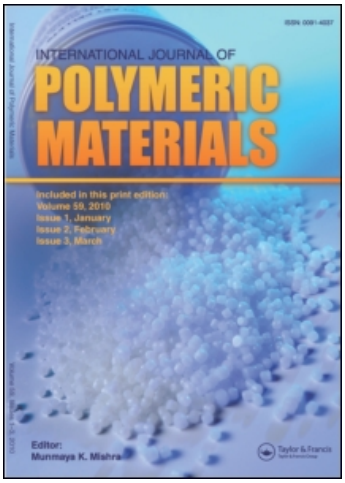

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Organic Chemistry of Macromolecules

Charles G. Overberger[a]; K. N. Sannes[a]
[a] Department of Chemistry and the Macromolecular Research Center, The University of Michigan, Ann Arbor, Michigan

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Organic Chemistry of Macromolecules†

CHARLES G. OVERBERGER and K. N. SANNES

Department of Chemistry and the Macromolecular Research Center, The University of Michigan, Ann Arbor, Michigan 48104

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Polymers as reagents in organic synthesis may offer certain advantages over low molecular weight reagents. Examples given include cyclization reactions, Dieckmann reactions, acylation and alkylation of active methylene esters, intrapolymeric reactions, hydrogenation of cyclic olefins, and hydrolysis of esters. The influence of cooperative effects and hydrophobicity on the self-acceleration and allosteric effects on some of these reactions is discussed.

1 POLYMERS AS REAGENTS IN ORGANIC SYNTHESIS

1.1 Introduction

One of the first applications of a macromolecule as a "solid support" in organic synthesis has served to revolutionize the field of peptide fabrication. Condensing specific sequences of amino acids onto a growing peptide, which is attached to an insoluble polymer, has, at least in principle, changed peptide synthesis from one of tedious, multi-faceted separations to a procedure which has been automated. No further account[1] of this field will be given in this report except for certain studies which apply to a topic under discussion.

Instead, this section of the report contains what we thought to be novel applications of polymeric reagents in synthetic organic chemistry. No attempt at inclusiveness was made.

1.2 Proximity effects

1.2.1 *Dilution or separation of reactants* The ability to control the relative rates of competitive reactions in a given system constitutes a good portion of

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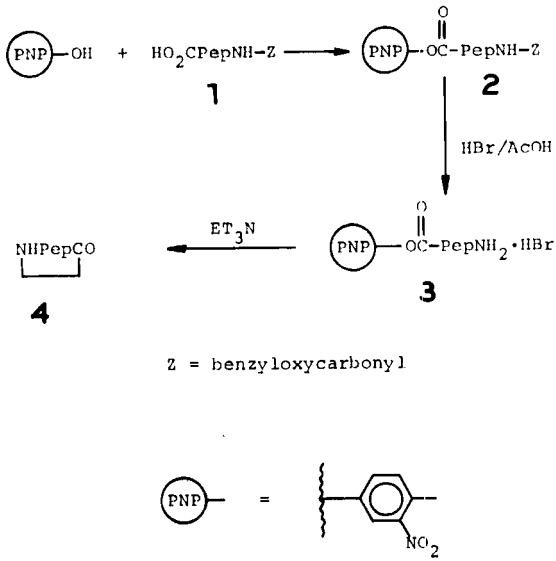
successful synthetic chemistry. In particular, cyclization reactions are successful only when the rate of the intramolecular ring closure reaction dominates over the rate of the competing intermolecular coupling reaction. Traditionally, high dilution of the reactant has been used to reduce the rates of the latter reaction and, thereby, increase the amount of desired cyclic product which is formed. Obviously there are limitations involved with this method.

Another method of limiting the rate of intramolecular reactions consists, in theory, of anchoring each molecule to be cyclized to a functional group along a polymer chain at intervals that preclude intermolecular (strictly speaking it would now be "intrapolymeric") reactions.

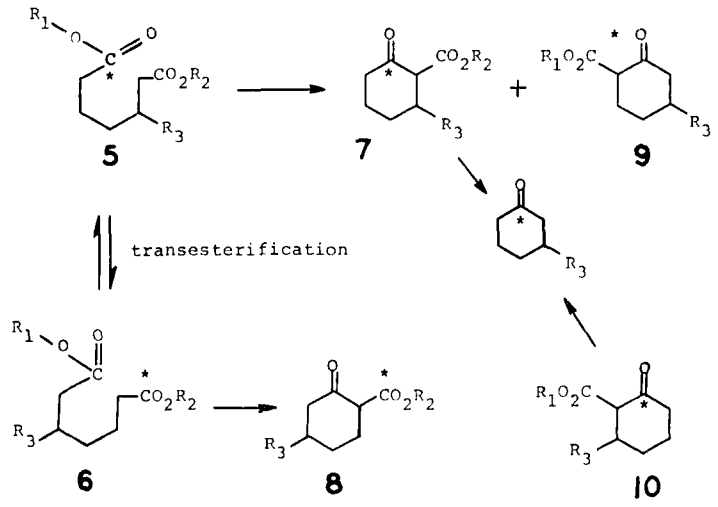
The ring closure of amino acids attached to a polymeric support establish the feasibility of this type of reaction.[2,3] As outlined in Scheme I, the N-blocked



SCHEME I

amino acid, **1**, is attached to poly-3-nitro-4-hydroxystyrene to form the polymer ester **2**. Removal of the blocking group affords amine **3** which, upon treatment with triethylamine, undergoes cyclization with simultaneous separation of the newly formed cyclic peptide, **4**, from the insoluble macromolecular support.

Another study has demonstrated the feasibility of performing Dieckmann reactions on diesters which are bonded to solid supports.[4] Potassium salts of ^{14}C labeled pimelate half esters were reacted with either chloromethylated polystyrene or benzyl chloride to form compounds **5a**–**5e** (Scheme II). Treatment of **5a**, **5c** or **5e** with base afforded 15–46% yields of cyclized products.



5a – 10a,	R_1	P	*p*-$C_6H_4CH_2$–,	R_2	$C(C_2H_5)_3$,	R_3	H
5b – 10b,	R_1		$C_6H_5CH_2$–,	R_2	$C(C_2H_5)_3$,	R_3	H
5c – 10c,	R_1	P	*p*-$C_6H_4CH_2$–,	R_2	$C(C_2H_5)_3$,	R_3	C_2H_5
5d – 10d,	R_1		$C_6H_5CH_2$–,	R_2	$C(C_2H_5)_3$,	R_3	C_2H_5
5e – 10e,	R_1	P	*p*-$C_6H_4CH_2$–,	R_2	C_2H_5,	R_3	H

* ^{14}C label.

SCHEME II

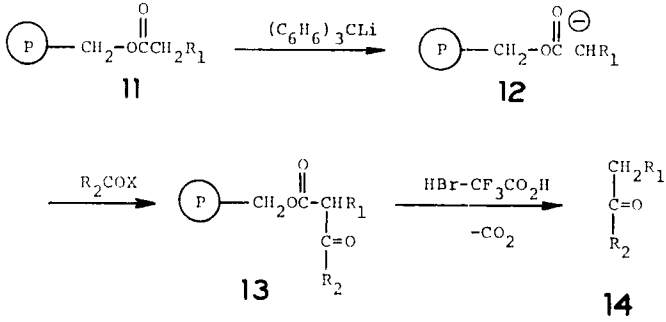
There are additional advantages offered with the solid support system that warrant discussion. For example, **5b** affords two cyclic products **7b** and **9b** when treated with base, which contain the alkyl and benzyl esters, respectively (Table I). Also, the group R_3 occupies a different relative position on the ring in **7b** and **9b**. When **5a**, for example, is reacted with base one might still form **9a**. However, in this case the cyclic compound **9a**, is still attached to the polymer support and is separated from **7a** during the filtration of the polymer from solution. This eliminates the need for the separation of the two similar keto esters as is the case in reactions **5b** and **5d**. Evidently a hindered ester (triethylcarbinyl in **5a** and **5c** instead of ethyl as in **5e**) must be used to prevent transesterification. Once this has been done, this procedure can serve very nicely in the preparation of specifically labeled ring compounds. As mentioned, this method can probably be extended to systems with various ring sizes.

TABLE I

Dieckmann reactions of diesters bonded to solid supports

Starting diester	Combined mole % of **9** and **10**	Relative amounts of non-benzylic ester products % **7**	% **8**
5a	—	99.69	0.31
5b	10	98.30	1.70
5c	—	97.25	2.75
5d	21	96.80	3.2
5e	—	mixture	

Successful acylation[5] and alkylation[6] of active methylene esters bound to polymer supports have been reported. Again, in the acylation of active methylene esters the competing self-condensation reaction is made negligible by attaching the active esters at intervals sufficiently large so as to prevent intrapolymeric reactions. Another undesired reaction, diacylation, is also prevented, presumably for similar reasons. The reactions in Scheme III



P = polystyrene

R_1 = H, C_6H_6

X = Cl, OCR_2

11a	**14a**,	R_1	C_6H_5,	R_2 p-$NO_2C_6H_4COCl$
11b	**14b**,	R_1	C_6H_5,	R_2 p-BrC_6H_4COCl
11c	**14c**,	R_1	C_6H_5,	R_2 $(\alpha$-$C_{10}H_7CH_2CO)_2O$
11d	**14d**,	R_1	H,	R_2 p-$NO_2C_6H_4COCl$

SCHEME III

[10]

provided a single ketone in each case (see Table II). Analogous reactions without the polymer support resulted in several ketonic compounds. Reasonably, it was observed[5] that if the concentration of ester bound to the polymer becomes too high the intrapolymeric reactions begin to interfere. The successful acylation reactions employed 0.1–0.3 mmoles of ester/gram of polymer and competing reactions were evident at concentrations of 1.5–2.0 mmol of ester/gram of polymer.

TABLE II

Ketone formation from esters bonded to solid supports

Starting material	R_2COX	Product	Yield, %	Recovered starting acids, %
11a	p-$NO_2C_6H_4COCl$	**14a**	43	40
11b	p-BrC_6H_4COCl	**14b**	40	45
11c	$(\alpha$-$C_{10}H_7CH_2CO)_2O$	**14c**	40	55
11d	p-$NO_2C_6H_4COCl$	**14d**	20	45

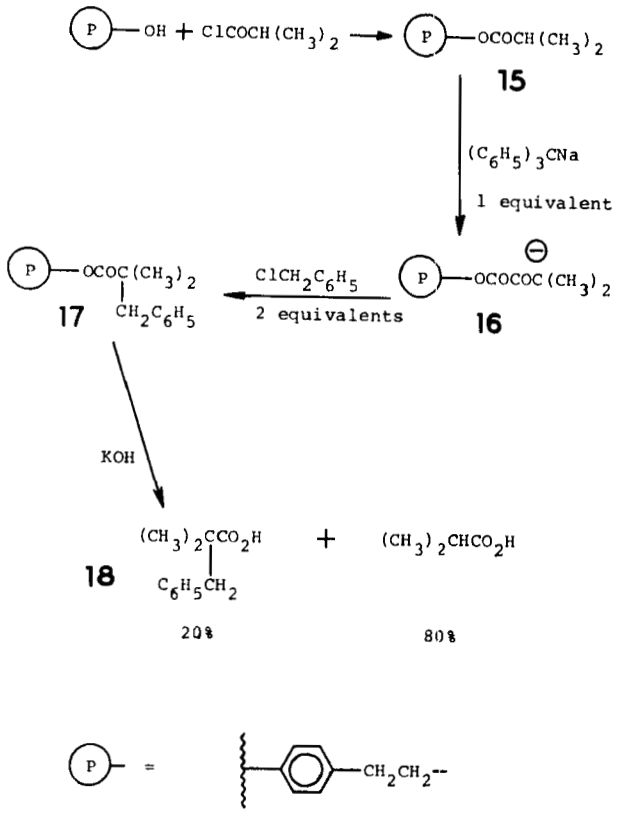
The alkylation of isobutyric acid[6] which was esterified onto a nonbenzylic support, as depicted in Scheme IV, afforded only benzyldimethyl acetic acid (**18**) and unreacted isobutyric acid in 20 and 80% yields, respectively.

1.2.2 *Forced combination of moieties connected to the same macromolecule* In contrast to the effect obtained by separating interreactive molecules by bonding them remotely on a macromolecule, a system could, in principle, be constructed with two types of molecules held in close proximity in order to promote this "intrapolymeric" reaction. In practice this type of proximity effect is involved in the reaction outlined in Scheme V.[7] A small percentage (2.3–25%) of chloromethylated polystyrene groups were esterified with a limited amount of an enolizable acid, **19**, and the remainder of the groups with

TABLE III

Ketone formation from enolizable esters bonded to solid support

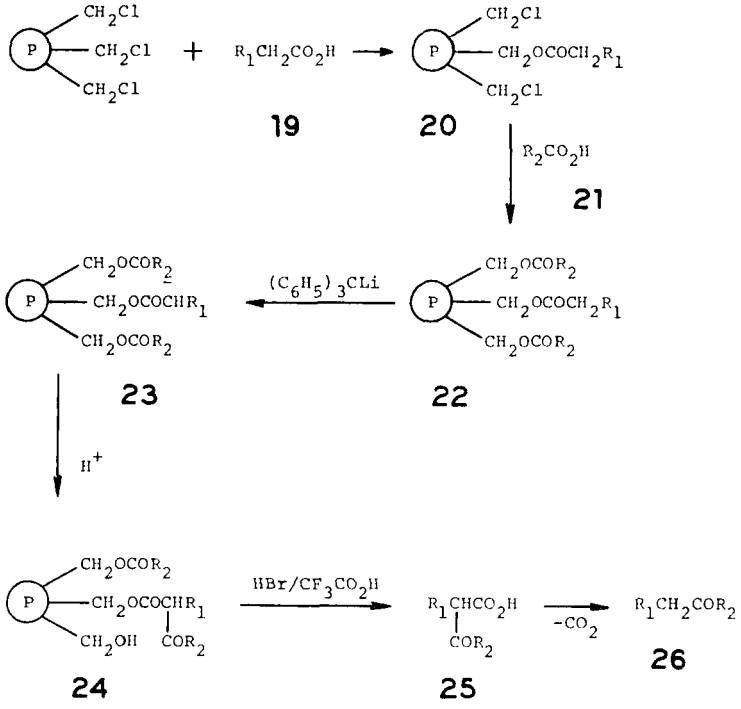
Enolizable acid	Non-enolizable acid	Yield, %	Analogous reaction in solution
$CH_3(CH_2)_6CO_2H$	p-$ClC_6H_4CO_2H$	35	30
$C_5H_5CH_2CO_2H$	$C_6H_5CO_2H$	45	—
$C_6H_5(CH_2)_2CO_2H$	$C_6H_5CO_2H$	85	42
$CH_3(CH_2)_4CO_2H$	$C_6H_5CO_2H$	95	—
$C_6H_5(CH_2)_2CO_2H$	p-$ClC_6H_4CO_2H$	85	20



SCHEME IV

a nonenolizable acid, **21**, to give the mixed ester **22**. The addition of base results in internal condensation to form **24** which after esterolysis and decarboxylation provided *only* ketone **26** and starting acids **19** and **21**. Analogous reactions under similar conditions but without the polymer support lead to a more complex mixture of products. The intrapolymeric nature (**23** → **24** in Scheme V) of the reaction is evidenced by the fact that no ketone was observed when two batches of polymeric esters—one with an enolizable and one with a nonenolizable ester—were reacted and worked-up under conditions similar to those used for **22**. This scheme is in line with the fact that a larger ratio of **21**:**19** in **22** results in higher yields.

In the solid-phase synthesis of peptides, side-reactions limit the length of the peptide chain that can be obtained in purified form.



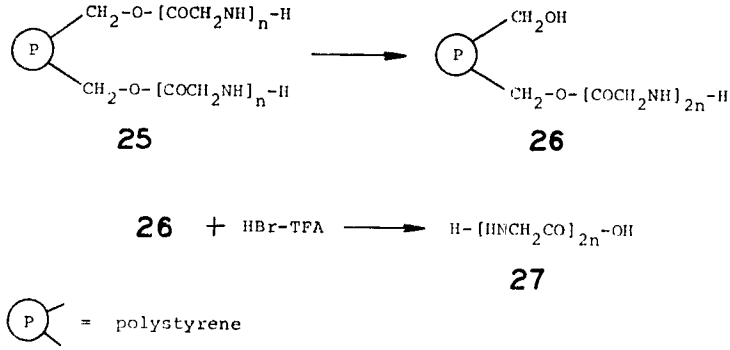
R_1	$CH_3(CH_2)_5$,	C_6H_5,	$C_6H_5CH_2$,	$CH_3(CH_2)_3$	
R_2	*p*-ClC_6H_4,	C_6H_5			

SCHEME V

A "chain doubling" reaction (Scheme VI) has been reported in the Merrifield synthesis of peptides.[8] The distance between peptide residues on **25** is such that a reaction much like that of condensation of two esters on one polymer chain occurs. This study used 0.5 to 0.7 mmole of peptide/gram of peptide resin. A lower concentration of peptide residues would tend to reduce chain doubling. Other factors that may prove to be important in these intrapolymeric reactions are the chain length of peptide, the nature of the polymeric leaving group, degree of cross-linking of the support, and the solvent system.

1.3 Cooperative effects

The fact that juxtaposition of reactive moieties can be "insured" if they are pendant groups of a polymer is the basis for another advantage of polymeric reagents which has been labeled "cooperative effects". In a polymer the



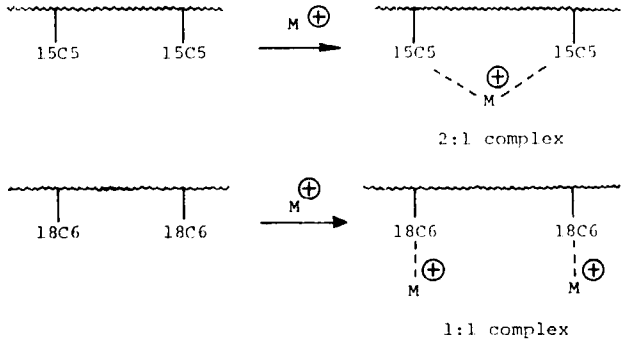
SCHEME VI

reaction of two pendant groups with a third molecule from the solution mimics a bimolecular reaction which has much less stringent entropy requirements than a termolecular reaction in solution. This phenomenon has been called on to explain kinetic results of enzyme prototype systems.

Recently, complexes of alkali metal ions with either polymeric crown ethers or their monomeric crown ether analogs were studied.[9]

The cyclic monomeric ethers 15C5 and 18C6 (monomeric models of P-15C5 and P-18C6, Scheme VII) form 2:1 and 1:1 complexes, respectively, with fluorenylpotassium in THF and solid KCNS complexes and the evidence points toward the same stoichiometry in this study. This difference in the stoichiometry of 15C5 and 18C6 ethers has been reasonably attributed to the difference in ring diameter of the two ethers.

The generally larger ratios of polymeric to monomeric complexing strength in the 15C5 ether systems compared to the same ratios in the 18C6 system



SCHEME VII

[14]

(Table IV) is expected if two crown units complex with each alkali metal ion in the former system. Two crown units are held in close proximity in the polymer and the 3 unit complex would form more readily than would the 3 unit complex in the 15C5 monomeric system. Since the complex is of a 1:1 nature in the 18C6 system the difference between polymeric and monomeric systems would not be expected to be as great.

TABLE IV

Ratios of complexing abilities of analogous polymeric *versus* monomeric crown ethers with alkali metal ions

Cation	Poly-15C5/15C5	Poly-18C6/18C6
Li^+	>10	6.2
Na^+	2.3	1.6
K^+	3.8	1.1
Rb^+	6.4	1.1
Cs^+	19.7	

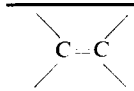
1.4 Selectivity of substrate

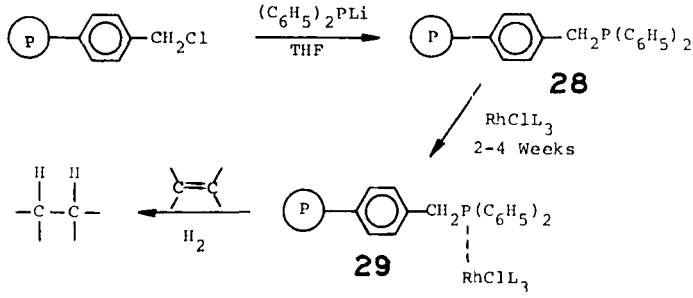
1.4.1 *Size* If the active site of a macromolecule is located inside a semi-ordered insoluble polymer, it is not difficult to visualize a situation in which the rate of reaction of substrates would depend on their ability to gain access to this active site. For example, the size of a molecule would certainly be one such factor.

A system such as is described above has been reported in a study in which the selective hydrogenation of olefins was demonstrated with a polymer-supported rhodium(I) catalyst.[10] As Table V shows the relative rate of reduction of cyclic olefins depends upon the size of the ring when the reducing agent is coupled to a macromolecule, **29**, while this effect is not evident with tris(triphenylphosphine)chlororhodium(I) (see also Scheme VIII).

1.4.2 *Hydrophobicity* In aqueous solutions, apolar bonding between two hydrophobic molecules has been shown to be a factor in increasing the rate of hydrolysis of esters by polymeric catalysts.

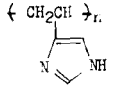
TABLE V

	Beads, **29** relative rates	$RhClL_3$ 2.5 mmol
Cyclohexene	1	1.0
Cyclooctene	1/2.54	1.0
Cyclododecene	1/4.45	1/1.5
Δ^2-Cholestene	1/32	1/1.4



SCHEME VIII

The esterolytic action of the synthetic, macromolecular catalyst, poly-4(5)-vinylimidazole (PVIm) has been investigated.[11] The rate of the PVIm-catalyzed esterolysis of a long-chain ester (S_{12}^-) was *ca.* 10^3 times as fast as that of the monomeric imidazole (Im) catalyzed esterolysis of the same ester.[12] These esterolytic rates were found to be critically dependent on the chain length of the acid portion of the substrate and one the solvent composition. The bulk of the rate enhancement was thus attributed to apolar association of catalyst and substrate.



PVI m

Im

During the study of the PVIm and Im-catalyzed hydrolyses of S_n^- in varying vol% ethanol–water a very interesting autocatalytic or *accelerative kinetic pattern* was observed (see Figure 1). The rate of the reaction continuously increased so that at 75% completion the rate was *ca.* 5 times faster than the initial rate.

By observing the deacylation rates of the polymeric acyl imidazoles from the hydrolysis of S_n^- (see Scheme IX), it was noted that for the cases exhibiting the accelerative behavior, deacylation was the rate-determining or slow step. This demonstrates again the influence of apolar bonding on the rates of esterolysis. The acylated polymer is more hydrophobic than the non-acylated polymer.

Table VI shows the surprisingly large dependence of the deacylation rate on the chain length of the acyl group. This observation is rationalized by considering formation of a polysoap-like structure as the polymer is increasingly acylated with long-chain groups.[13]

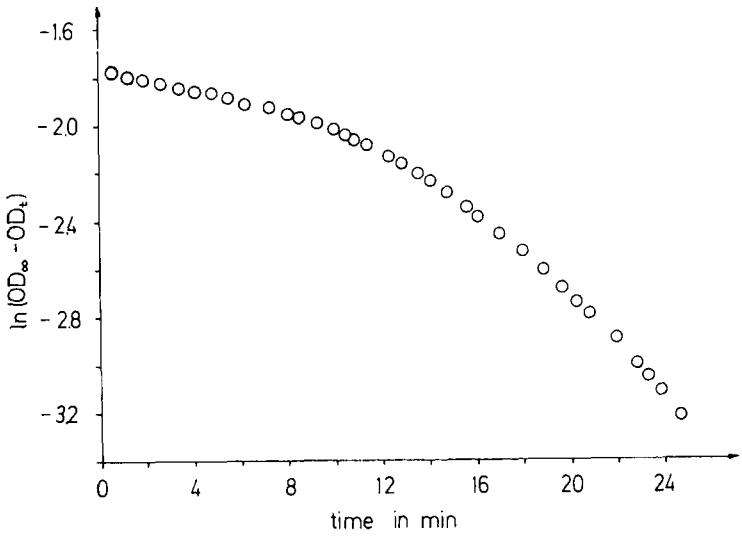
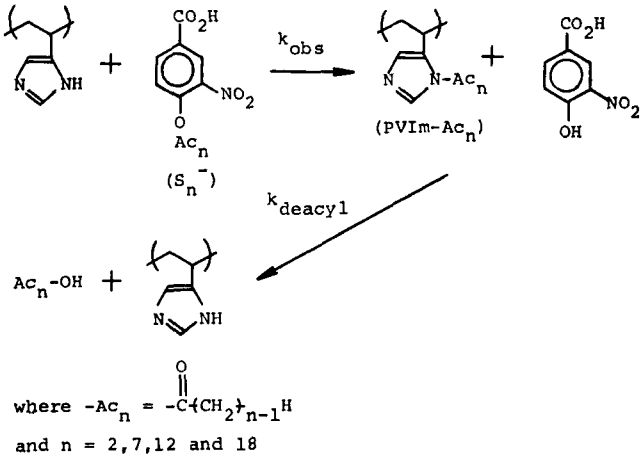


FIGURE 1 Pseudo-first-order plot of the esterolysis of cyclododecene catalyzed by poly-4(5)vinylimidazole (PVIm) shows accelerative kinetic pattern. 40 vol.perc. C_2H_5OH in H_2O, [PVIm] = 5.0×10^{-4} mol/dm^3, [S_{12}^-] = 5.0×10^{-5} mol/dm^3, $\mu = 0.02$, TRIS = 0.02 mol/dm^3, pH = 8.0, 26°C. [Reprinted with permission from *J. Am. Chem. Soc.*, **95**, 6014 (1973).]



SCHEME IX

[Reprinted with permission from *J. Am. Chem. Soc.*, **95**, 6014 (1973).]

[17]

TABLE VI

First-order rate constants for hydrolysis (acylation) and deacylation reactions[a]

[Reprinted with permission from *J. Am. Chem. Soc.*, **95**, 6014 (1973).]

Substrate	k_{obs}(min^{-1})[b]	Intermediate	k_{deacyl}(min^{-1})[c]
S_2^-	0.022	PVIm-Ac_2	0.250
S_7^-	0.013	PVIm-Ac_7	0.242
S_{12}^-	0.090[d]	PVIm-Ac_{12}	0.041
S_{18}^-	0.500[d]	PVIm-Ac_{18}	0.006

[a] 40 Vol% ethanol-water, $\mu = 0.02$, pH = 8.0, 26°C.
[b] [PVIm] = 5.0×10^{-4}mol/dm^3 [S_n^-] = 5.0×10^{-5}mol/dm^3.
[c] Determined for >90% deacylation completed; deacylation is accelerative.
[d] Accelerative kinetic behavior, k_{obs} at *ca.* 75% reaction.

Figure 2 shows the effect of varying percent dodecanoylation of PVIm on the hydrolyses of S_7^- and S_2^-. Particularly for S_7^-, the rate increased as the content of long-chain, acyl groups increased. These results served to elucidate the cause of the accelerative behavior.[13] Progressive intramolecular micellarization occurring along the polymer chain creates an increasingly nonpolar

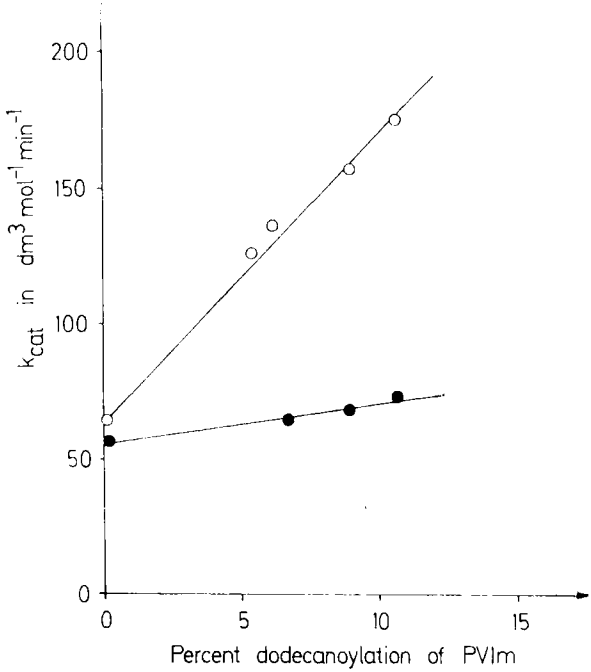


FIGURE 2 Catalysis by PVIm-Ac_{12} of S_7^- (○) and S_2^- (●). 33 vol.perc. C^2H_5OH in H_2O, $\mu = 0.02$, TRIS = 0.02 mol/dm^3, pH = 8.0, 26°C. [Reprinted with permission from *J. Am. Chem. Soc.*, **95**, 6014 (1973).]

molecule. This results in an enhancement of the apolar association of substrate and catalyst. Undoubtedly, a conformational change accompanies this process of polysoap formation which is evidenced through the kinetics of the hydrolysis reaction.

The situation described above may be considered conceptually similar to the *allosteric effect* displayed by certain enzyme systems.[14] The catalytic function of enzymes may be affected and controlled by interaction with small molecules, not only directly, at the active site, but also indirectly, at distant, secondary allosteric sites. Generally, a conformational change accompanies the observation of the allosteric phenomena. The accelerative behavior is evidence of a conceptually similar occurrence in the case of the synthetic, macromolecular catalyst, PVIm.

Hydroxylamine is known to be more than 10^5 times as effective as water in acyl transfer from acetyl imidazole.[15] Figure 3 demonstrates the effect of added hydroxylamine on the accelerative behavior. The acceleration is diminished with increasing hydroxylamine content in the system; this can be explained by a decrease in the concentration of the intermediate. Eventually, the accelerative behavior is completely eliminated, indicating that the intermediate is being destroyed at a faster rate than the substrate is being hydrolyzed.

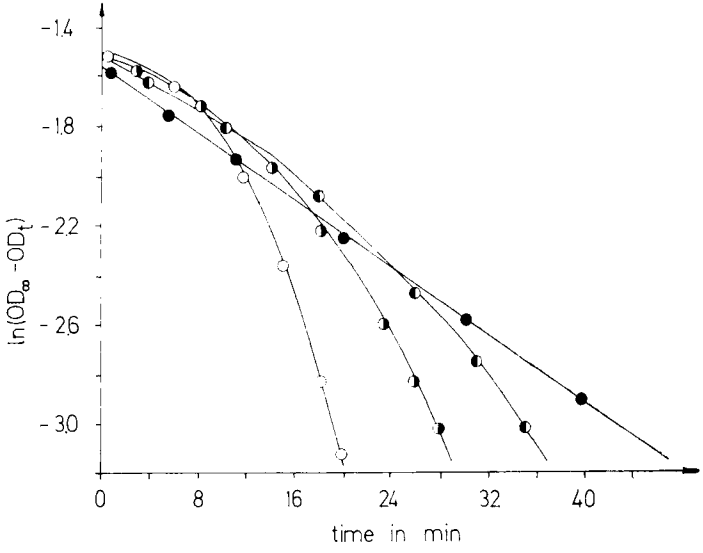


FIGURE 3 Effect of increasing concentration of hydroxylamine on accelerative behavior. 40 vol.perc. C_2H_5OH in H_2O, [PVIm] = 5.0×10^{-4} mol/dm^3, [S_{12}] = 5.0×10^{-5} mol/dm^3 (○), with [NH_2OH] = 3.0×10^{-4} mol/dm^3 (◑), 4.5×10^{-4} mol/dm^3 (◐), 11.1×10^{-4} mol/dm^3 (●).

The viscosity of PVIm in varying vol% ethanol–water (Figure 4) indicates a contraction of the macromolecule in low and high ethanol compositions.[16] Shrinkage of the polymer coils in low ethanol content might be the result of intra- and intermolecular nonpolar interactions, whereas its shrinkage in

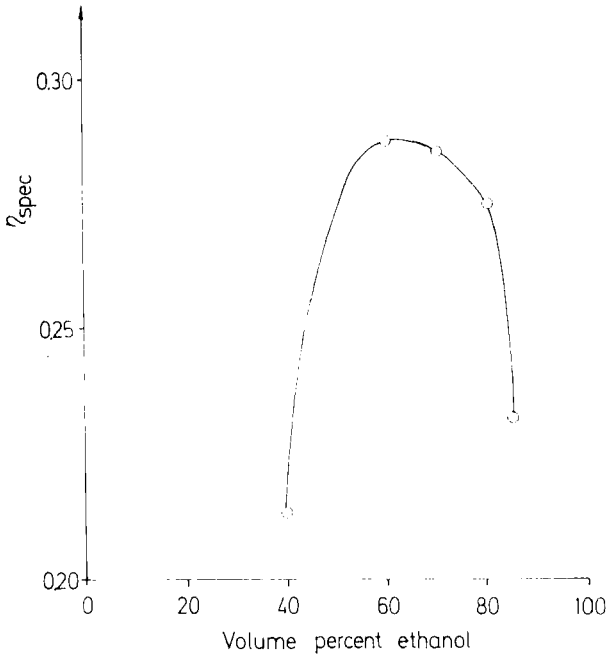


FIGURE 4 Solution viscosity of poly-4(5)-vinylimidazole as a function of ethanol/water composition. [PVIm] = 4.229 g/dm^3, μ = 0.02, 26°C. [Reprinted with permission from *J. Am. Chem. Soc.*, **93**, 3222 (1971).]

solvents of high methanol content is ascribed primarily to intra- and intermolecular hydrogen bonding.[16] Figure 5 shows the kinetic manifestation of this conformational process for the hydrolysis of *p*-nitrophenyl acetate (PNPA) and *p*-nitrophenylheptanoate (PNPH).

1.5 Change in mechanism

The bromination of cumene with N-bromosuccinimide (NBS) in carbon tetrachloride results in the expected benzylic bromination product **33** and a dibromoproduct **34** (Scheme X). However, when poly-NBS, prepared by bromination of polymaleimide, was used as the brominating agent, a completely different set of products was obtained[17] as shown in Scheme X. This demonstrates another feature of macromolecular reagents; that of a

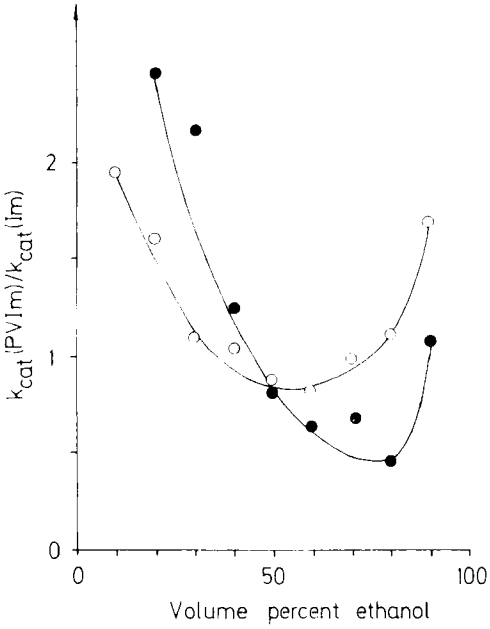


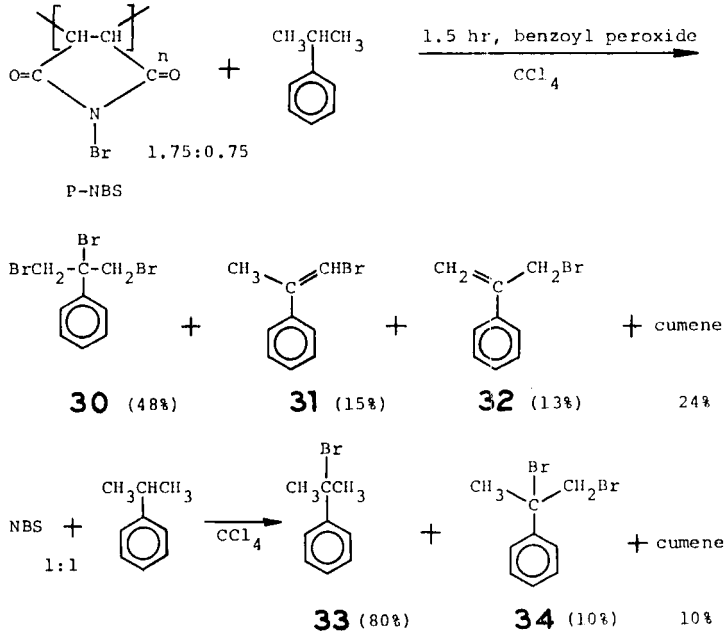
FIGURE 5 Ratios of rate constants of the poly-4(5)vinylimidazole (PVIm) and monomeric imidazole (Im) catalyzed solvolysis reactions of PNPA (○) and PNPH (●) as a function of the ethanol concentration in water at 26°C, pH ≈ 8, and μ = 0.02. [Reprinted with permission from *J. Am. Chem. Soc.*, **93**, 3222 (1971).]

change in mechanism (Scheme XI) upon anchoring the functional moiety to a large carrier molecule.

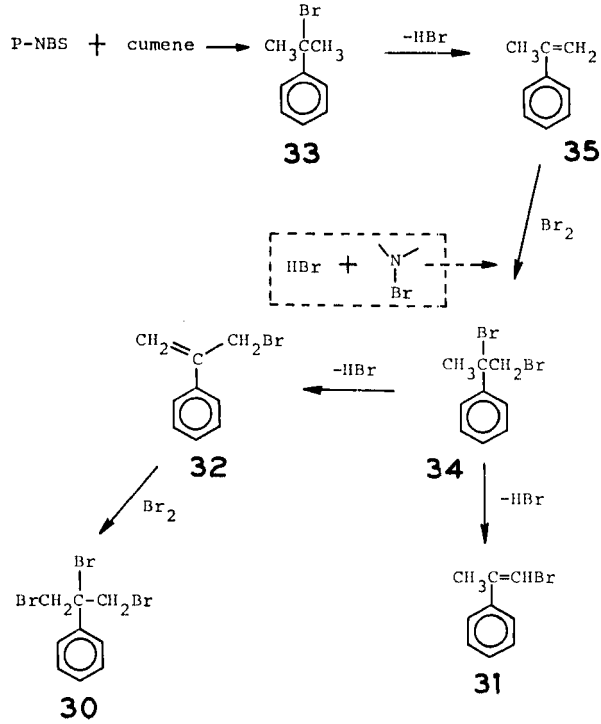
The polar medium provided by neighboring succinimide units in the polymer may be responsible for the (especially the repeated dehydrobromination) changed mechanism and different products obtained in NBS and poly-NBS brominations. This idea is substantiated by the fact that the bromination of cumene with NBS in a *more polar* solvent, acetonitrile, results in products similar to those obtained with poly-NBS in carbon tetrachloride.

1.6 Simple separation of polymeric reagent

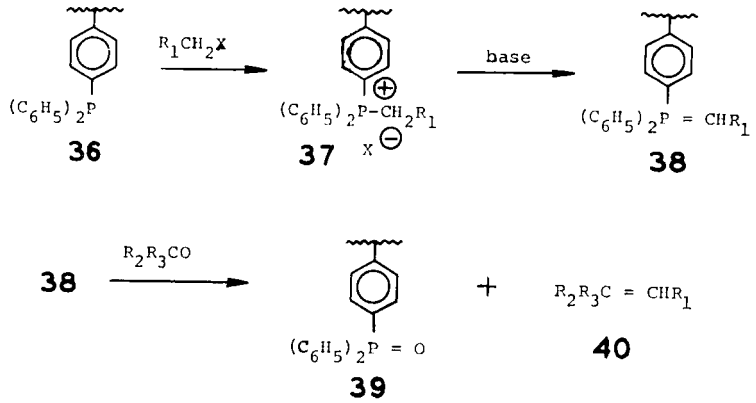
Polymeric phosphoranes have been prepared (Scheme XII) and reacted with carbonyl compounds to form olefins.[18] These Wittig reactions on polymeric supports afford product yields comparable to monomeric reactions but the removal of the phosphine oxide formed in the reaction is done by simply filtering the polymer to which the P–O unit (**39**) remains attached. This advantage is, in principle, one of ease in separation, much like solid phase peptide synthesis.



SCHEME X



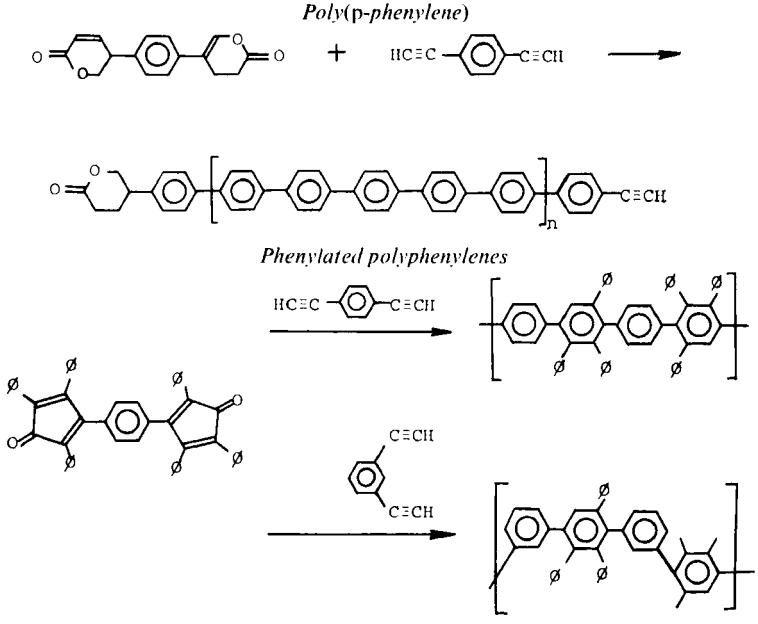
SCHEME XI



SCHEME XII [From Ref. 18]

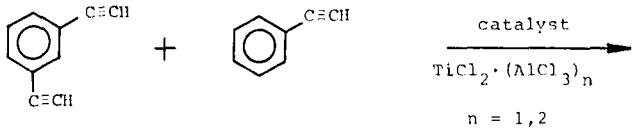
2 HIGH TEMPERATURE POLYMERS—POLYPHENYLS

It is not my purpose here to review the subject of polymers useful at high temperatures. Polyphenyls, of course, have always been attractive since they provide a structure which does not allow a low activation energy rate process such as oxidation or hydrolysis to be important. Included here are several examples of some recent syntheses of polyphenyls designed particularly to make them more soluble in organic solvents.[19-22]



[23]

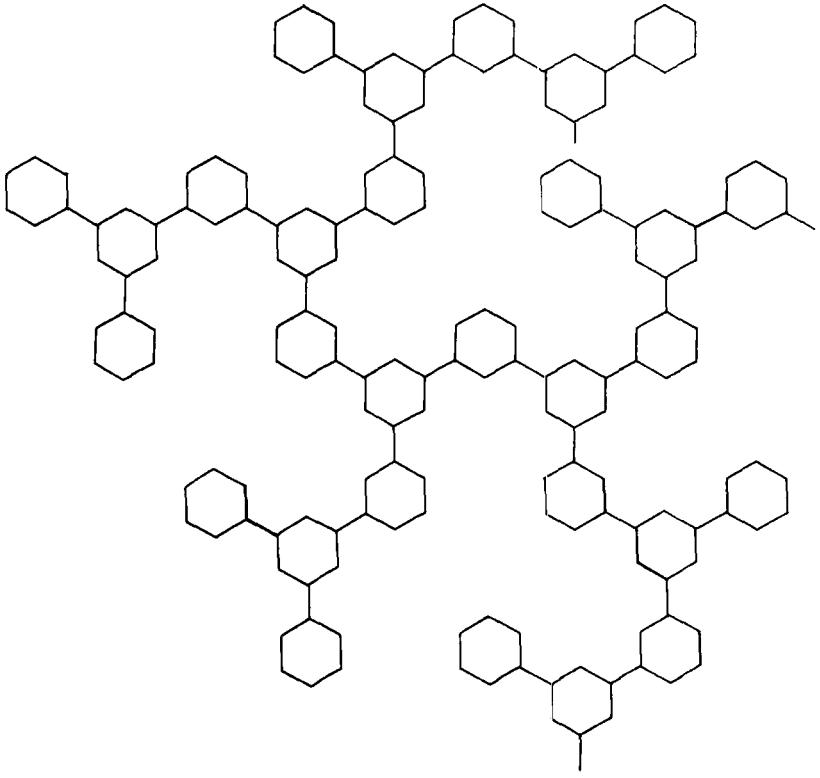
Branched chain polyphenyl



A B

A/B = 1.5 Ph = 70,000

Structure of polyphenylenes [From Ref. 22]



[24]

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