# Polymer-supported polymerization. A general technique for the preparation of novel beaded polymer supports

**Reza Arshady***
*Organisch-Chemisches Institut der TU Munchen, Lichtenbergstr. 4, 8046 Garching, W. Germany*
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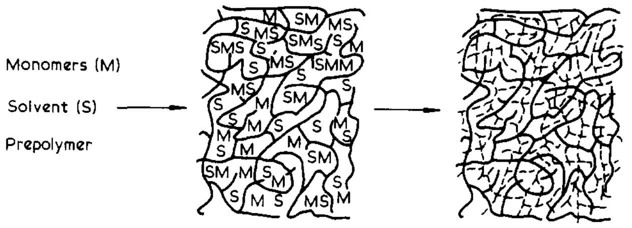
A new technique is described whereby the copolymerization of differentially soluble monomers is carried out after being absorbed onto the beads of a highly swellable dimethylacrylamide prepolymer support. The general applicability of the technique is demonstrated by the preparation of beaded multi-component resins incorporating (i) styrene, 2-hydroxyethyl methacrylate, and divinylbenzene, (ii) polyethyleneimine crosslinked by 1,4-(dichloromethyl)benzene, and (iii) palladium(II) coordinated by two or four isonitrile ligands, respectively.

**Keywords** Differentially soluble monomers; beaded prepolymers; copoly(styrene-2-hydroxyethyl methacrylate); polyethyleneimine; copoly(isonitrile-palladium)s

Crosslinked functional polymers are widely employed in affecting increasingly large number of chemical[1] as well as biochemical[2] transformations. These polymers, generally referred to as polymer supports or polymeric reagents, are obtained either by modification of preformed polymers (e.g., polystyrene[3a], polyacrylamide[3b] of polysaccharides[3c]) or preferably by incorporation of suitable functional monomers during the formation of the polymer[4]. In most cases the actual chemistry of the polymer-bound species may not be affected by the physical form of the polymer. However, regularly sized beaded resins obtained by suspension polymerization generally offer considerable practical advantages over amorphous materials. Many vinyl-based polymers composed of either water-insoluble[1,4a] or water-soluble[4b c] monomers are readily accessible through suspension polymerization. The latter technique is not, however, generally practicable for polymerization of differentially soluble monomers, nor can it be employed for polycondensation. Preparations of beaded, or particulate, polymers from differentially soluble monomers have been carried out employing a brine solution[5a], or carefully controlled precipitation polymerization[5b], respectively. In a previous communication[6] a new approach to this problem was reported in which copolymers of maleic anhydride were prepared within the beads of highly permeable resins based on dimethylacrylamide. This communication describes the general applicability of this approach for the preparation of polymeric materials of widely differing characteristics and composition.

The technique which may be termed 'polymer-supported polymerization' is best illustrated by *Scheme 1*, and is reminiscent of reinforcement processes widely employed in the rubber industry[7]. The given monomer mixture (including solvent, initiator, etc.) is shaken with a chosen beaded polymer support until the solution is completely absorbed by the polymer. The polymerization is then initiated and is allowed to continue to completion. The coagulated polymer beads are then gently stirred (or ground over a sieve) in a good solvent and the product is subsequently freed of powder-like materials by repeated decantations. In principle any swellable beaded polymer may be employed to form a new polymer within its matrix. In practice, one or another resin type may be preferred for reasons of availability, monomer and solvent compatibility, and its modifying effects on the newly formed polymer. For the present work a generally permeable dimethylacrylamide-based prepolymer was adopted. This polymer (**P1**) was prepared by suspension copolymerization of dimethylacrylamide and *N,N'*-hexamethylenediacrylamide (2, 5 mole %) according to a previously described general procedure[4c]. It shows an expanded volume of about 15 ml/g in a wide range of solvents including aqueous, protic, and aprotic organic solvents. This polymer is also readily permeated by low or high molecular weight substrates of widely differing nature, e.g., from styrene (**1**) to 2-hydroxyethyl methacrylate (**3**) on the one hand, and copolymers of maleic anhydride[6] and polyethyleneimine (**5**) on the other.



*Scheme 1* Polymer-supported polymerization: The illustration of the swollen prepolymer support is particularly intended to indicate the homogeneous (random) distribution of the monomer(s), and thus the embedded polymer, throughout the prepolymer matrix

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* Present address: Department of Chemistry, Imperial College, London SW7 2AZ, UK

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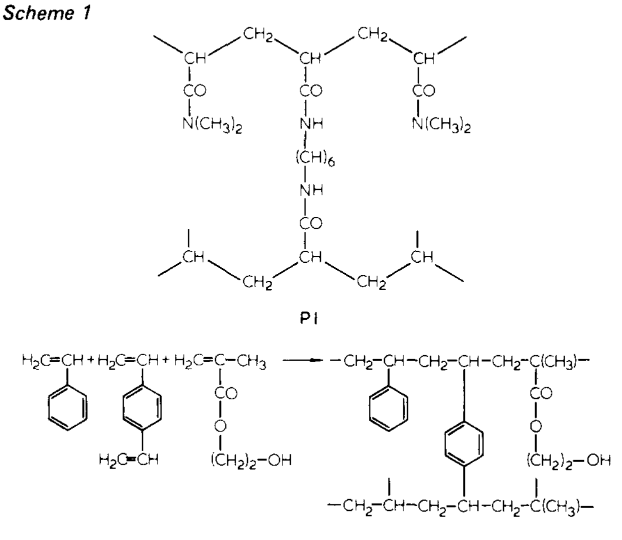
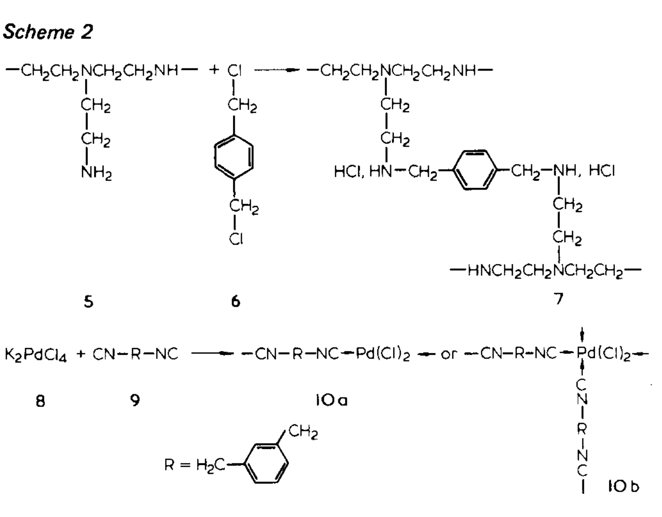
Highly permeable copolymers of styrene and divinylbenzene have also been developed and used for polymer-supported polymerization. Styrene-based prepolymers are, however, only suitable for systems involving hydrophobic substrates and solvents, e.g., the polymerization of tetracyanobenzene in nitrobenzene[8].

The general applicability of the new method is demonstrated here by the polymerization of three types of monomer mixtures as indicated in *Scheme 2*. This Scheme represents examples of free radical, condensation, and coordination polymerization, respectively. The schematic structure of the prepolymer **P1** and those of the embedded polymers **4**, **7** and **10** are shown separately, but the notations **P1/4**, **P1/7** and **P1/10** refer to the resulting multi-component beaded resins. For most free radical polymerizations (e.g., that of **1**–**3**) the prepolymer is swollen in the monomer mixture, and the polymerization is carried out in a manner essentially similar to those of the corresponding bulk or solution polymerizations. However, if the formation of the polymer takes place at a faster rate than the penetration of the monomer mixture into the prepolymer (e.g., in the preparation of **P1/10**), then more elaborate procedures are required as outlined below.

*Scheme 1*



*Scheme 2*



For the preparation of the multi-component resins represented in *Scheme 2*, polymerization conditions were empirically adjusted to achieve complete conversion of the monomers. (**5** is regarded as a monomer.) **P1/4** was obtained by swelling the prepolymer in the monomer mixture (**1**:**2**:**3** = 10:1.2:10, 5g/g prepolymer) containing 4% AIBN in chlorobenzene (5 ml/g prepolymer), followed by polymerization at 60°C for 15 h. For the preparation of **P1/7**, the prepolymer was shaken with **5** (50 mmol/g) in methanol followed by evaporation of the solvent. This was then mixed with **6** (3.5 mmol/g prepolymer) in dimethylformamide (10 ml/g prepolymer) and kept at 60°C for 3.5 h. The palladium containing resins **P1/10a** and **P1/10b** were prepared by shaking the prepolymer with **8** (1 mmol/g) in water, removal of the solvent, followed by mixing with **9** (1 or 2 mmol/g prepolymer) in chloroform. The copolymerization of **8** and **9**, as indicated in *Scheme 2*, takes place almost instantaneously. The resulting beaded resins **P1/10a** and **P1/10b** are completely stable in non-coordinating solvents such as water, methanol, and dichloromethane, but both **10a** and **10b** are gradually removed from **P1** in the presence of coordinating solvents such as dimethylformamide. However **10a** and **10b** can be permanently entrapped on **P1** in the presence of a complementary crosslinked matrix incorporating a relatively high content of divinylbenzene. (Details of these and similar metal derivatives prepared by polymer-supported polymerization will be subsequently reported.) The resulting multi-component polymers were allowed to swell in dimethylformamide (DMF) or dichloromethane (DCM), wet-sieved, and washed with DMF, dioxane, ether, and dried. Generally 90–100% of the expected polymeric products were obtained.

The expected structures of the multi-component resins **P1/4**, **P1/7**, and **P1/10** were confirmed by the increased weight of the prepolymer beads, elemental analysis, and/or infra-red (i.r.) spectroscopy. An i.r. spectrum of **P1/4** shows the characteristic absorptions of the embedded polymer (hydroxyl at 3400 cm$^{-1}$ broad, and carbonyl at 1710 cm$^{-1}$) as well as that of the prepolymer (tertiary amide at 1615 cm$^{-1}$). The bis-coordinated isocyano groups in **P1/10a** show a singlet at 2255 cm$^{-1}$, whereas the tetrakis-coordinated resin **P1/10b** shows a doublet with peaks at 2255 cm$^{-1}$ and 2215 cm$^{-1}$. (The free isocyano groups in **9** absorb at 2145 cm$^{-1}$).[9] Chlorine analysis of **P1/7**, before and after treatment with sodium hydroxide, indicates that all of the chloromethyl groups of **6** have (within experimental error) taken part in the expected crosslinking process. The crosslinking reaction is assumed to proceed mainly through the alkylation of the primary amino groups as indicated in *Scheme 2*, but concurrent alkylation of the secondary amino groups cannot be ruled out. The commercially available polyethyleneimine (**5**) has been extensively studied as an enzyme model[10]. The presently described resin **P1/7** provides a convenient and easy to handle polyimine derivative containing hydrophobic residues which are known to generally enhance the esterolytic activity of enzyme-like polymers[10].

## *Conclusions*

Impregnation of a highly permeable beaded polymer support by a given monomer mixture and subsequent polymerization of the monomers, provides a simple technique for the preparation of beaded multi-component polymeric materials. The method, termed 'polymer-supported polymerization', is very simple, generally applicable, and does not involve any of the technical requirements of suspension polymerization. Although not an alternative to routine suspension polymerization, the technique provides a highly practical means of preparing beaded resins when direct bead polymerization is not practicable for one reason or another. The general applicability of the method has been demonstrated for free radical, condensation, and coordination polymerizations, and it should be equally applicable for ionic polymerization. The preparations of various beaded resins including those of potential interest in transition metal catalysis and enzyme-like polymers have been described. The overall physico-chemical, and particularly the topochemical, behaviour of the embedded polymer clearly may be influenced by the nature of the prepolymer matrix. This often provides an additionally versatile means of tuning the properties of a given tailor-made functional polymer by the appropriate choice of a suitable prepolymer support. The dimethylamide structure of the presently described prepolymer (**P1**) generally widens the solvent compatibility of the embedded polymer, and is thought to have favourable topochemical effects in, for example, acylation reactions.

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# Electrochemical synthesis of polyacetylene tetrachloroferrate $[CH(FeCl_4)_y]_x$ and tetrachloroaluminate $[CH(AlCl_4)_y]_x$

**J. Przyłuski, M. Zagórska, K. Conder and A. Proń**
*Department of Chemistry, Technical University of Warsaw,* 00 664 *Warsaw, Noakowskiego* 3, *Poland*

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Polyacetylene can be electrochemically oxidized in $LiClFeCl_3$ nitromethane and $LiClAlCl_3$ nitromethane solutions to give a highly conducting (500 $ohm^{-1}$ $cm^{-1}$) polymer exhibiting *p*-type conductivity. The limiting composition obtainable in the electrolysis can be expressed by the following formula: $[CH(MCl_4)_{0.05}]_x$ where M=FeAl.

**Keywords** Conducting polymers; polyacetylene; electrochemical doping; acceptor type doping; metal halide doping

## *Introduction*

Graphite and other macromolecular systems like polyacetylene, poly(*para*phenylene), polypyrrole, etc., are known to react with a large variety of electron accepting compounds to give a whole class of new materials exhibiting high electrical conductivity. There are several groups of compounds that are able to convert polyacetylene into 'an organic metal' and they can be classified as follows: halogens[1], main group transition metals halides[2–4], noble gas fluorides[5] and protonic acids[6].

The chemistry of the 'doping reaction' involves the oxidation of the polymer chain with the concomitant introduction of a proper amount of anions stabilizing the polycarbonium cation formed. This result can be achieved by chemical oxidation or electrochemically through anodic oxidation. The latter process has been successfully applied to the fabrication of light weight rechargeable batteries[7]. Recently some work on the introduction of anions of protonic acids into polyacetylene has been carried out, e.g. $ClO_4^-$,[7] $PF_6^-$.[8] In this communication we report that the introduction of $Fe^{3+}$ and $Al^{3+}$ chloroanions into polyacetylene can be achieved through anodic oxidation of $(CH)_x$ in $LiCl–FeCl_3$ and $LiCl–AlCl_3$ solutions.

## *Experimental*

*Materials and reagents.* The polyacetylene used in all the experiments was prepared using a modification of the method from Ito *et al.*[9] The $(CH)_x$ film had a *cis:trans* ratio of approximately 1:1. $FeCl_3$ and LiCl were vacuum dried at 100°C and 150°C respectively for one hour. A.C.$_3$ was kept over calcium chloride and then vacuum distilled. For

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