

POLYMER-SUPPORTED GRIGNARD REAGENT AND ITS USE IN THE FUNCTIONALIZATION OF POLYMER

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ABSTRACT

Polymeric Grignard Reagent (PGR) based on the chloromethylated poly(ST-co-DVB) resin has been prepared by means of anthracene-magnesium complex in THF (Anth-Mg-THF), and polymer matrix with long polymethylene spacer was synthesized via the coupling reaction between PGR and α, ω -dibromoalkanes. Based on the studies of factors affecting the coupling, such as catalyst, reaction time, the length of spacer etc., this paper offers the optimal reaction conditions and three typical experiment procedures. The mechanism for the formation and coupling reaction of PGR are also discussed.

INTRODUCTION

Crosslinked polystyrene resin has received considerable attention as supports for polymeric catalysts and reagents. Gel-typed styrene-co-divinylbenzene resin is often used as matrix of phase-transfer catalysts (PTC) with all the unusual advantages of retention, isolation and recovery; but the attachment of catalytic species to the polymeric matrix near the main chain decreases the catalytic activity of PTC greatly^[1]. Investigations show that spacer-modified polymeric catalysts have a higher activity than those without alkylene spacers. In the literatures, spacer-modified resins were obtained by attaching spacers to the resin via oxygen ether bond^[1a], amide bond^[2], and ester bond^[3] etc., or by copolymerization of monomers with spacers attached by carbon-carbon bond^[1b] directly. We had attempted Friedel-Crafts alkylation on ST-co-DVB resin by allowing dibromoalkane to react with styrene resin in the presence of $\text{AlCl}_3\text{-SnCl}_4$ ^[4], but these tests failed to succeed. This paper will offer a novel and convenient method for introducing spacers by carbon - carbon bond onto the crosslinked styrene

resin. The preparation of PGR does make far-reaching senses in the functionalization of polymer.

EXPERIMENTAL

1. Preparation of polymeric Grignard Reagent (PGR) on chloromethylated polystyrene resin ($P-CH_2Cl$, where P -stands for crosslinked polystyrene resin)

In a three-necked round-bottomed flask (250ml) were added 0.1g of magnesium turnings, 0.005g of iodine, 0.6g of anthracene and 80ml of THF (refluxed over benzophenone and sodium before use). The reaction mixture was stirred at refluxing temperature under dry nitrogen atmosphere till a grey-coloured liquid was obtained.

After 2.0g of $P-CH_2Cl$ (Cl : 1.5 mmol/g, 80–100 mesh) was added rapidly, the reaction mixture was further stirred at 80–82°C under the same condition for nearly one day. By now, the polymeric Grignard Reagent was obtained.

2. Preparation of poly (ST-co-DVB) resin with long bromoalkyl chains

After the addition of catalytic amount of inorganic salt (e.g. : $CoCl_2$, Li_2CuCl_4 etc.) into the PGR system, a mixture of 15ml THF and V ml of alkylene dibromide (i.e. $Br(CH_2)_nBr$; $n=3, V=5$; $n=4, V=6$; $n=6, V=8$; $n=10, V=11$) was charged dropwise into the flask through a separatory funnel with a pressure-equalizing tube. The reaction mixture was stirred at 85–88°C for 4–6hrs. 15ml of 15–20% H_2SO_4 was used to quit the reaction. The mixture was filtered off, washed successively with warm benzene or toluene, water-methanol (2 : 1), water-methanol (1 : 2), methanol and ether. The crude product was extracted with ether for 60hrs, and the slight-yellow final product was obtained.

Determination of bromine content in poly (ST-co-DVB) resin was proceeded according to the literature procedures^[5]. Polymer-supported bromine was converted into elementary bromine by combustion and oxidized to bromate with hypochlorite, and finally determined iodometrically. The unreacted chlorine in chloromethyl groups does not interfere the determination.

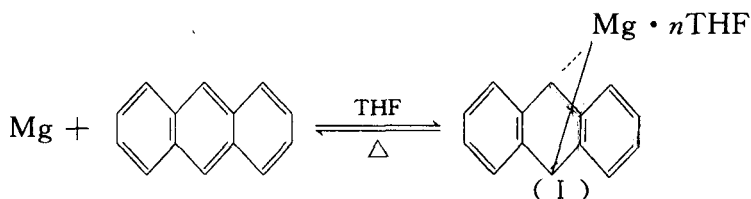
3. Preparation of Li_2CuCl_4 and $LiCuCl_2$

In equal molar ratio for $LiCl$ and $CuCl_2$ and 2 : 1 ratio for $LiCl$ and

CuCl_2 , the chlorides were added into absolutely dry THF and stirred for about 20min at r. t. under dry atmosphere till a blue solution of complex LiCuCl_2 and orange-red solution of Li_2CuCl_4 in THF were obtained.

RESULTS AND DISCUSSION

Insolubility of chloromethylated resin and magnesium turnings in THF prevents them from coming into contact with each other, so PGR is not easily obtained via general method. However metallic magnesium can be activated by reacting with anthracene in an equilibrium way^[6] to produce a highly active organometallic complex (I), which is soluble in THF and thus accessible to the $\text{P-CH}_2\text{Cl}$:



The formation of PGR can be identified by the IR spectra and the elementary analysis of chlorine. After the transformation of PGR and the followed acidic aqueous quenching, the characteristic IR peak of $-\text{CH}_2\text{Cl}$ group at 1272cm^{-1} and 680cm^{-1} diminished greatly.

A series of bromoalkyl-spacer-modified poly (ST-co-DVB) beads has been synthesized in the following pathway, the product has strong characteristic C-Br IR bands at 1270cm^{-1} and $620-640\text{cm}^{-1}$. Refer to Fig. 1 and Table 1.

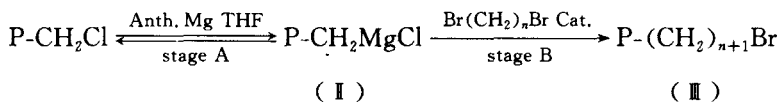


Table 1 Bromine content in $\text{P-(CH}_2)_n\text{Br}$ ($n=3,4,6,10$)

n	3	4	6	10
Br^* (mmol/g)	0.52	0.43	0.51	0.47

* identified by IR and XPS spectra, determined by the elementary analysis of bromine
reaction time: 4hrs at stage B, temperature (in oil-bath): $80-88^\circ\text{C}$

1. The mechanism for the coupling reaction of PGR

Coupling reaction of low-molecular Grignard Reagent RMgX can be

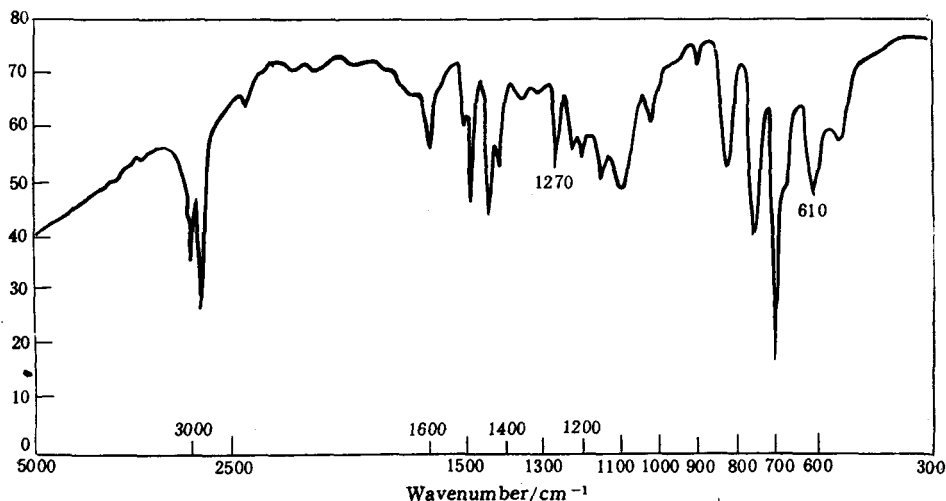
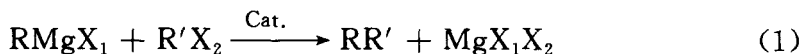


Fig. 1 The IR spectra of poly(ST-co-DVB) with ω -bromobutyl spacer

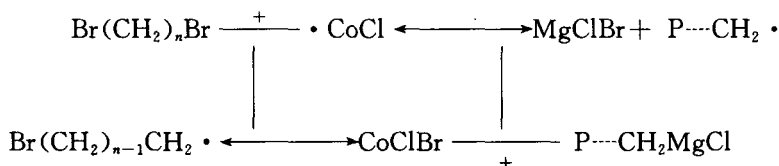
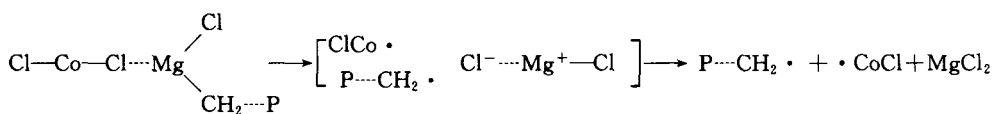
depicted as follows:



Where R, R' stands for alkyl group and X for Br or Cl.

The mechanism of the coupling reaction had been described to follow a radical pathway analogous to a single electron-transfer way, and perhaps one of the most detailed studies involved the reaction with benzophenone.^[7]

When the catalytic quantities of CoCl_2 were added to the PGR system containing excess alkylhalides, CoCl_2 in the solution acted as initiator to produce radicals. The catalytic cycle is illustrated as follows. The capture of radicals may destroy the coupling reaction. Of course, the typical experiments should proceed under the protection of a dry inert gas.



2. Factors affecting the coupling reaction of PGR

(1) Temperature

The coupling reaction of PGR performed at a high temperature condition in our tests, whereas it has been generally accepted that reaction (1) proceeds fast at low temperature. The reasons for this phenomenon may exist in the mechanism for the formation and reaction of PGR. Low temperature (below 78°C) makes the thermolysis and formation of radicals uneasy, but the temperature above 90°C leads to a vigorous refluxing of THF, and brings the disadvantage to the formation of complex (I) for the equilibria run in reverse direction. On the other hand, the radicals become relatively unstable under high temperatures resulting in the enhancement of unfavourable coupling activities of PGR (I) and PGR (IV) (as depicted below), the bromine content in resin is reduced because of further reactions between bromoalkyl spacer and relatively activated PGR. The evidence has been demonstrated by data in Table 2.

The existence of multicomponent gets the system temperature to rise above the boiling point of THF, and the favourable coupling temperature is 85–88°C. These results are identified with details in Table 2.

Table 2 Effect of temperature on the coupling reaction of PGR

Temperature ^{a)} (°C)	5–10	25	50–78	85–88	90–95
Br ^{b)} (mmol/g)	0.00	0.00	0.00	0.43	0.24

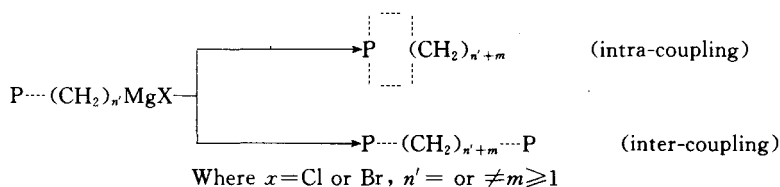
a) at stage B, reaction time: 4hrs, catalyzed by CoCl₂

b) identified by IR and XPS spectra, determined by the elementary analysis of bromine, only identified by IR spectra when without Br

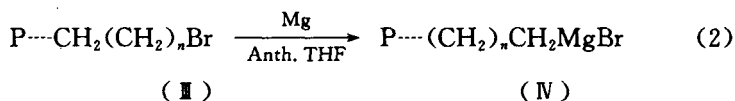
(2) Reaction time and the length of spacer.

Reaction time and the length of spacer influence the amount of bromine contained in the modified resin beads as shown in Table 3. Explanations could be made from the coupling reactions of PGR.

Unfavourable coupling reactions of PGR can be depicted as:



As shown in the compound (I), methylene group of PGR is near the polymer backbone and not so movable, thus intra-coupling reactions of PGR (I) are hindered. The unfavourable inter-coupling of PGR with the value of n less than 3 could be ignored for solid polymeric resin beads can not contact well with each other. Bromopolymethylene groups on the end of spacer in compound (II) could form another PGR (IV) by reacting with unreacted magnesium, i. e. :



Long spacer makes the methylenemagnesium bromide group more freely and active, so the intra and/or inter coupling reactions and reaction (2) take place. Within the short period of reaction time, contracting of PGR with dibromoalkane win the advantage over coupling reactions of PGR, while couplings surpass the former action within a long reaction time. By adding excess dibromoalkane and controlling the reaction time at stage B, the unfavourable reactions could be minimized.

Table 3 Effect of reaction time and the length of spacer on the coupling reaction of PGR

n	3	3	3	6	6	10	10
Time ^{a)} (hr)	1	4	10.5	3	12.5	3—3.5	7
Br ^{b)} (mmol/g)	0.27	0.52	0.48	0.51	0.10	0.47	0.00

a) at stage B, temperature: 85—88°C, catalyzed by CoCl_2

b) identified by IR and XPS spectra, determined by the elementary analysis of bromine, only identified by IR spectra when without Br

(3) Catalyst

Halides of transition metal (e. g. : CoCl_2 , CuCl , FeCl_3 etc.) can catalyze the coupling reaction of RMgX with $\text{Br}(\text{CH}_2)_n\text{Br}$, and they follow an analogous radical-producing pathway (see above), Their catalyses on the coupling reaction of PGR could be in an analogous mechanism. Catalytic effect of a few halides of transition metal with a similar constitution on the reaction of PGR are illustrated in Table 4.

Table 4 Effect of different transition metal halides as catalyst for the coupling reaction of PGR

Catalyst	/	CoCl ₂	CuCl ₂	CuCl	Li ₂ CuCl ₄	LiCuCl ₂
Br* (mmol/g)	0.00	0.52	0.57	0.55	0.59	0.46

* at stage B, reaction time, 4hrs, temperature, 85–88°C, n=3

identified by IR and XPS spectra, determined by the elementary analysis of bromine, only

identified by IR spectra when without Br

According to the results in Table 4, the catalytic activity order is: $\text{Li}_2\text{CuCl}_4 > \text{CuCl}_2 > \text{CuCl} > \text{CoCl}_2 > \text{LiCuCl}_2$. The optimal catalyst is Li_2CuCl_4 in the view of catalytic effect. CoCl_2 , CuCl_2 is often used, but its catalytic efficiency is lower than that of Li_2CuCl_4 and its easy hydrolysis brings much inconvenience to operation.

By the reaction of bromoalkyl spacer-modified resin with triphenylphosphine, spacer-modified polymeric phosphonium salts which acts as PTC have been synthesized successfully. These polymeric phosphonium salts have characteristic IR peaks at 1100cm^{-1} and 1440cm^{-1} , as the former literature reported.

Keywords:

Grignard reagent; Polymer supported; Anthracene; Coupling reaction; Crosslinked polystyrene

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