

Studies on the Chloromethylation of Polystyrene Resins

NIYAZI BICAK, GUNES KOZA and YUSUF YAGCI

Istanbul Technical University, Department of Chemistry, Maslak, Istanbul 80626, Turkey

ABSTRACT

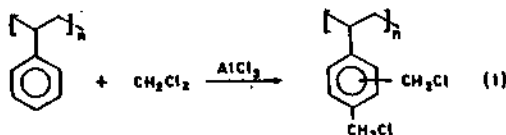
Chloromethylation of polystyrene polymers and its crosslinked resins by Fridel-Crafts alkylation with CH_2Cl_2 was described. Reactions conducted above 0°C resulted in crosslinking with CH_2 linkages between phenyl rings of polystyrene. The effect of reaction time on the chlorine content and swelling properties of the resin was also demonstrated.

KEY WORDS: Polystyrene, Chloromethylation, Crosslinked resin.

INTRODUCTION

Functional polymers based on crosslinked polystyrene beads have been object of many researches over the past three decades, since Merrifield's report on solid phase peptide synthesis in 1963¹. Chloromethylated polystyrenes are key intermediates in preparation of various functional polymers and may be prepared by several ways. One is the use of chloromethyl methyl ether in the presence of Lewis acid catalysts². The carcinogenic chloromethyl methyl ether and its far more potent carcinogenic contaminant *bis* (chloro-methyl) ether have deterred to the use of the method. Preferred methods involve generation of chloromethyl methyl ether *in situ* in order to lessen the hazard³. Chlorination of poly (*p*-methylstyrene) with commercial aqueous sodium hypochlorite bleach solutions and a phase transfer catalyst provides a much safer route⁴.

Polymerization and copolymerization of *p*-chloromethyl styrene is another method but suffers from the high costs. Alternatively, Fridel-Crafts alkylation of polystyrenes with CH_2Cl_2 affords a convenient procedure for preparation of the functional derivatives of polystyrene.⁵ However, applicability of



the method depends critically on the availability of functionalization without side reactions.

The present paper reports results, demonstrating that controlled halomethylation of polystyrene polymers and copolymers by Fridel-Crafts alkylation with CH_2Cl_2 can be achieved by optimizing time-temperature parameters.

EXPERIMENTAL

Materials

All chemicals except dichloromethane were analytical grade and used without further purification. Dichloromethane was purified by conventional drying and distillation procedures. Linear polystyrene, having viscosity $\eta_{inh} = 1.2$ dl/g in toluene at 30°C , was obtained by emulsion polymerization. Polystyrene beads were prepared according to the described procedure⁶ and by this method macroporous and crosslinked with 2% of divinyl benzene resin was obtained.

Chloromethylation of the polystyrene resin

10 g of styrene-divinyl benzene resin was placed in 50 mL of CH_2Cl_2 in a flask and shaken overnight. The flask was put in an ice-bath as external cooling. 3 g of finely ground AlCl_3 was added to the flask and an outlet tube with anhydrous CaCl_2 was attached to the flask for the evolution of HCl gas. The reaction was conducted for 7 h with stirring. Aliquot samples were taken from the mixture at intervals in order to test the ratio of chloromethylation. After filtration, the reaction mixture was poured into 50 mL water in order to remove unreacted AlCl_3 . The beads were filtered and washed with excess water. However, the product was still brown due to the presence of AlCl_3 adducts in the structure. The product was then put into 50 mL of 5% HCl solution to avoid possible hydrolysis of chloromethyl groups and stirred until the color becomes white. Finally, the beads were filtered, washed with excess water and dried. The same procedure was applied also to the test samples.

Chloromethylation of linear polystyrene

5 g of polystyrene was dissolved in 50 mL of CH_2Cl_2 and 1.5 g of AlCl_3 was added to the solution. The same procedure was then followed as above.

Chloromethylation of the model compound

21.5 g (0.16 mol) of *tert*-butyl benzene was put into 100 mL of dry CH_2Cl_2 and 6.7 g of AlCl_3 was added to the flask connected with HCl delivery tube. The mixture was stirred at 0°C for 3.5 h. The reaction content was then poured into 150 mL of cold water to remove unreacted AlCl_3 . After washing several times with cold water, organic layer was separated and dried with anhydrous CaCl_2 . The remaining CH_2Cl_2 was evaporated and finally unreacted *tert*-butyl benzene was distilled out in the range of $165\text{--}173^\circ\text{C}$ under atmospheric pressure (2.3 g). The mixture was then fractionated at 25 mm-Hg.

Chloromethylation ratios in all experiments were followed by determination of chlorine contents according to the standard method⁷.

Swelling Experiments

Weighed amount of (ca. 200 mg) resin samples which are chloromethylated in different reaction times and a given solvent were placed in a sample bottle. The sealed samples were left for 7 days at room temperature. The solvent was then decanted, the pearls superficially dried with tissue and reweighed in order to determine their swollen weight and thus I/Q .

Where, $I/Q = (\text{Dry weight}) / (\text{Swollen weight} - \text{Dry weight})$

RESULTS AND DISCUSSION

There are two important points in the chloromethylation experiments which need to be considered carefully: crosslinking and irregular multisubstitu-

tion reaction on the phenyl ring. The former occurs as a result of inter- and intramolecular Friedel-Crafts alkylation hence forming CH_2 links between and in the polymer chains, respectively. From the practical point of view, this reaction is more important than the latter since it results in decrease of the number of the chloromethyl functionality. Furthermore, it contributes also indirectly to the decrease of the reactivity of the functional groups due to greater difficulty in penetration of the solvent into polymer networks.

The chloromethylation of linear polystyrene with excess CH_2Cl_2 using AlCl_3 at temperatures above 0°C proceeds with significant secondary crosslinking reactions as concluded from the formation of insoluble material. Thus, 0°C became the temperature of the choice for chloromethylation of both linear and crosslinked polystyrene. The chlorine contents of the polymers versus the chloromethylation time is illustrated in Figure 1. It is interesting to note that chlorine contents of the resin increase more dramatically than that of linear polystyrene. This behavior may be attributed to the restricted mobility of phenyl rings of the crosslinked resin, thus preventing the already incorporated chloromethyl groups to participate in the next Friedel-Crafts reaction instead of methylene chloride. Taking this into account, the gradually reduced solubility of linear polystyrene during the reaction and increase of the ratio of aliphatic to aromatic C-H stretching vibrations in the

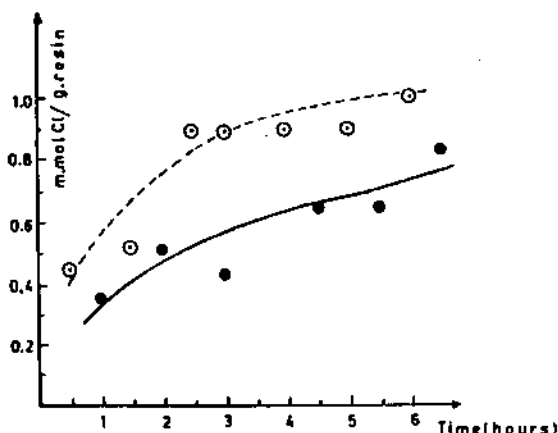


Fig. 1. Chlorine contents of chloromethylated products of polystyrene (●) and polystyrene crosslinked with 2% divinyl benzene (○) versus reaction time.

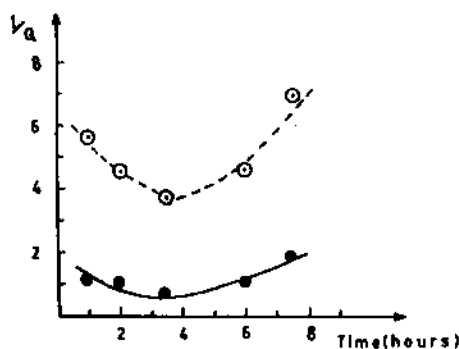


Fig. 2. Swelling properties of the chloromethylated polystyrene resins at different reaction times in toluene (●), and CH₂Cl₂ (○).

region of 2850–2950 cm⁻¹ are tentatively attributed to the existence of methylene bridges between phenyl rings of the polystyrene chains.

The effect of the chloromethylation on the swelling of the crosslinked resin in two solvents was also studied. As can be seen from Figure 2, the swelling property of the resin in CH₂Cl₂ was even improved to certain extent, due to similarity of the incorporated group and solvent. This is an additional advantage of using CH₂Cl₂ as the chloromethylation agent and solvent which is capable of penetrating the polymer and swelling the surface of the resin. Hence, the reaction can proceed inside swollen layer and high yields are attainable. On the other hand, after further chloromethylation, the conversion yield remains rather low, if the interaction between polymer and solution is minimum, i.e. the swelling of the resin is

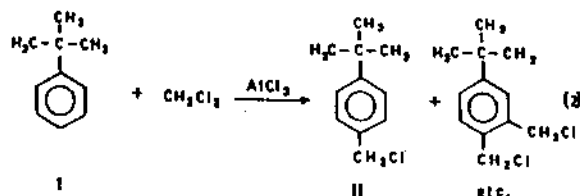
TABLE I. Distillation Fractions of Chloromethylation Products of the Model Compound^a

Fraction	Boiling Range (°C at 25 mm-Hg)	Weight Percentage (%)	Chlorine Content (%)
I	125–132	11.9	3.6
II	133–139	30.7	18.9
III	139–180	20.7	21.3
Residue	—	14.7	1.0

^aFor conditions see experimental section

reduced. In this case chloromethylation is restricted to the uppermost surface layer of the resin.

Tert-butyl benzene was chosen as model compound so as to predict substitution positions and numbers on the phenyl ring in polystyrene.



Boiling points, yields and chlorine contents of the fractions of alkylation reaction carried out under similar conditions are collected in Table 1. Fraction II was assigned to *p*-chloromethyl derivative from its boiling point (139–142 °C/27 mm-Hg), chlorine content (calc. 19.45 %) and IR spectra (C–Cl stretching vibration was observed at 740 cm⁻¹). Fraction III contains a mixture of low molecular weight condensation products with CH₂ bridges and higher chloromethylated compounds. IR spectra of this mixture shows a very intense aliphatic C–H and C–Cl stretching vibration bands at 2860–2970 and 760 cm⁻¹, respectively. *Ortho*-substitution is prevented by the bulky *tert*-butyl group. On the basis of these observations, one or two chloromethyl groups are incorporated to the phenyl ring of polystyrene. However, multisubstitution is not very important as far as the practical application is concerned. The second chloromethyl group may also participate in subsequent functionalization. Attempts for the chloromethylation at higher temperatures yielded mainly solid products with very low content of fraction II (only 3.5%) when the reaction was carried out at room temperature.

In order to introduce some functionalities to the chloromethylated polystyrene resin, which was obtained by the described procedure, several experiments were performed. The chloromethyl groups were successfully converted into cyanomethyl, thiocyanomethyl and hydroxymethyl groups by the methods given in the literature⁸. CN and SCN groups were identified by the characteristic IR bands at 2220 and 2250 cm⁻¹, respectively.

In conclusion, these results illustrate the versatility of the method and practical applications for the chemical modification of crosslinked polystyrene resin appear feasible.

REFERENCES

1. R.B. Merrifield, *J. Am. Chem. Soc.* **85**, (1963) 2149
2. K.W. Pepper, H.M. Paisley and M.A. Young, *J. Chem. Soc.*, (1953) 4097
3. G. Olah, W.S. Togyesi, "Friedel-Crafts and Related Reactions", Wiley-Interscience, Vol. 2, New York, 1964, pp. 659-784
4. S. Mohanraj and W.T. Ford, *ACS Polym. Preprints* **5** (1986)
5. Dow Chemical Co., *Brit. Pat.* 677, 350, Aug. 13, (1952)
6. A. Akar and H. Ersen, *Eur. Polym. J.* **19**, (1983) 279
7. A.I. Vogel, "A Textbook of Inorganic Quantitative Analyses," Longmans, London, 1961, p. 809
8. J.M.J. Frechet, M.D. Smet and M.J. Farral, *J. Org. Chem.* **44** (1979) 1774

Received: 12 July 1989

Accepted: 6 November 1990