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Convenient Synthesis and Free-Radical Copolymerization of p-Chloromethylstyrene

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ABSTRACT

p-Chloromethylstyrene, a useful monomer for a starting material in preparation of functional polymers, is conveniently synthesized by the chloromethylation of 2-phenylethyl bromide followed by dehydrobromination. This procedure is simpler and the yield is higher than those of methods previously described. Radical copolymerizations of this compound with styrene and methyl methacrylate were studied at 60°C. From the copolymerization with styrene, Q and e values for p-chloromethylstyrene were calculated as Q = 1.13 and e = -0.58. Similarly, the copolymerization parameters with methyl methacrylate were obtained as Q = 1.16 and e = -0.69.

INTRODUCTION

Chloromethylated polystyrene has been widely used as a starting material of many functional polymers [1-3]. However, in most cases, chloromethylated polystyrene was synthesized by the chloromethylation of copolymer of styrene and divinylbenzene in heterogeneous system [4]. Therefore, the distribution of reactive functional group in this polymer chain may not be uniform throughout.

It seems that the easiest way of overcoming this disadvantage is to use chloromethylstyrene as a monomer which can be readily homopolymerized or copolymerized with vinyl monomers. Unfortunately, commercially available chloromethylstyrene is a mixture of the meta and para isomers. For this reason, polymers obtained from this monomer do not possess precisely the expected structure. It is obvious that these polymers are not very satisfactory for the investigation of the relationship between structure and function.

In spite of this situation, reported syntheses of the para isomer [5, 6] gave low yield and were, moreover, tedious and expensive. Recently Arshady et al. [7] reported a high yield synthesis; however, their process is quite complex and in addition needs radical chlorination of p-ethyltoluene by sulfuryl chloride. This chlorination gives many products, and it is not easy to isolate the desired product from the reaction mixture by ordinary distillation. In this paper, we will present a simpler and less expensive method to synthesize p-chloromethylstyrene.

It is a curious fact that very little work has been reported on the characteristics of p-chloromethylstyrene in spite of its important uses. The monomer reactivity ratio of chloromethylstyrene can be found only in one literature source [8], and the source of this datum is given as a private communication. Moreover, the handbook does not tell which isomer (ortho, meta, para) was examined. Therefore, we studied the copolymerization of p-chloromethylstyrene with styrene and methyl methacrylate under radical conditions and calculated copolymerization parameters of this compound.

EXPERIMENTAL

Synthesis of 2-Phenylethyl Bromide

In a 1 liter three-necked flask fitted with a stirrer and reflux condenser, were placed 244 g (2 mole) of 2-phenylethyl alcohol and 500 ml of 47% hydrobromic acid. This mixture was refluxed for 15 hr. Then the acidic layer was discarded, and the organic layer was washed with water and dried. Distillation of the resulting crude oil gave 340 g (92%) of 2-phenylethyl bromide; bp 95-97°C/11 Torr (uncorrect.) (lit. [9] bp 99°C/15 Torr).

Chloromethylation of 2-Phenylethyl Bromide

2-Phenylethyl bromide (444 g, 2.4 mole) was dissolved in 200 ml of carbon disulfide in a 1 liter three-necked round-bottomed flask equipped with a stirrer, gas inlet tube, and a reflux condenser. Anhydrous zinc chloride (50 g) and paraformaldehyde (60 g) were added to the flask in three separate portions during the course of reaction. Hydrogen chloride was bubbled into the reaction mixture with rapid stirring for 20 hr at 35-40° C. The lower phase of the reaction mixture was soluble in water. The organic layer was washed with water, diluted sodium carbonate, and again with water. After being dried with anhydrous sodium sulfate, the carbon disulfide was distilled from the product, and the unreacted 2-phenylethyl bromide was recovered by distillation at a pressure of about 10 Torr.

The product, a mixture of o- and p-(2-bromoethyl)benzyl chloride was obtained by distillation, bp 90-94° C/2 Torr. The mixture was dissolved in 200 ml of petroleum ether and the solution was chilled overnight in a refrigerator. The remaining liquid was decanted, and obtained solid was recrystallized twice from 200 ml of petroleum ether. The yield was 238 g (51%); mp 48-50°C (lit. [6] mp 48-50° C). Gas chromatography of obtained compound showed one peak (Carbowax 20M, 10%, Celite 545, 1 m, 160 C, H_2). The ^{1}H-NMR spectrum showed 2.97-3.64 ($-CH_2CH_2Br$), 4.47 ($-CH_2Cl$), and 7.19 ppm (aromatic protons).

Synthesis of p-Chloromethylstyrene

A 9.2 g (0.4 mole) portion of sodium metal was carefully added to 700 ml of tert-butyl alcohol at 50° C. After all the metal reacted, the solution was cooled to the room temperature, and 93.4 g (0.4 mole) of p-(2-bromoethyl)benzyl chloride was added to the solution. The mixture was stirred at 35° C for 2 hr. Then the reaction mixture was poured into 2 liters of water and extracted with ether, and the extract dried with anhydrous sodium sulfate. The ether was removed under reduced pressure and the residue was distilled in the presence of p-tert-butyl catecohol to give 53.1 g (87%) of p-chloromethylstyrene, bp 81-83°C/2 Torr (uncorrect.) (lit. [7] bp 92°C/2 Torr). The IR spectrum of this compound agreed completely with that of p-chloromethylstyrene reported by Arshady et al. [7]. The ^{1}H-NMR spectrum is shown in Fig. 1.

Other Reagents

Styrene and methyl methacrylate used as comonomer were purified by ordinary methods and distilled in a stream of nitrogen just before use. Azobisisobutyronitrile (AIBN) used as a radical initiator was recrystallized twice from methanol. Other reagents were used after purification.

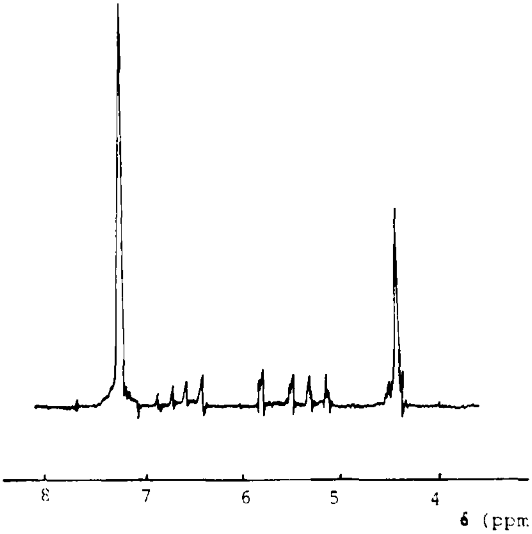


FIG. 1. NMR spectrum of p-chloromethylstyrene.

Copolymerization

Copolymerizations of p-chloromethylstyrene with styrene and methyl methacrylate were carried out in a sealed tube at 60° C. The required amounts of p-chloromethylstyrene, comonomer, AIBN, and benzene as solvent were charged into a Pyrex glass tube, which was then degassed under vacuum by conventional freezing and thawing technique and sealed off under vacuum. All copolymerizations were carried out with shaking under 10% conversion. After copolymerizations for a given time the tube was opened and its contents were poured into a large amount of methanol to precipitate the copolymer.

The resulting copolymers were then purified by the reprecipitation of the benzene solution with excess methanol.

The composition of the copolymers was calculated from their elementary analysis of chlorine. The monomer reactivity ratios (r_1 and r_2) were obtained by the Fineman-Ross method.

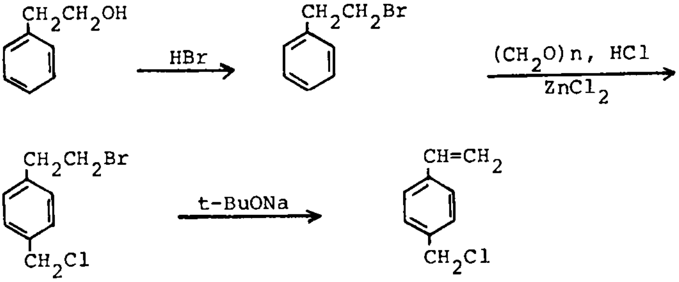
Instruments

IR spectra were recorded on a JASCO IRA-2 spectrometer. NMR spectra were recorded in carbon tetrachloride on 60 MHz Hitachi R-20B spectrometer with the use of tetramethylsilane as an internal standard.

RESULTS AND DISCUSSION

Synthesis of p-Chloromethylstyrene

The route of synthesis to p-chloromethylstyrene (I) is shown in Eq. (1).



I

(1)

The starting material for the synthesis of p-chloromethylstyrene was 2-phenylethyl alcohol. 2-Phenylethyl bromide was prepared from the reaction of 2-phenylethyl alcohol with hydrobromic acid. The next step in the reaction scheme was the chloromethylation of 2-phenylethyl bromide. Chloromethylmethyl ether has been often employed in the chloromethylation of aromatic compound. However, this reagent is known now to be highly carcinogenic. Therefore, we carried out this chloromethylation by use of paraformaldehyde and hydrogen chloride in the presence of zinc chloride. The chloromethylation of 2-phenylethyl bromide by this method yielded a mixture of ortho and para isomers of 2-bromoethylbenzyl chloride, from which pure para isomer could be easily isolated by the recrystallization twice from petroleum ether. Conversion to p-chloromethylstyrene was accomplished by treatment with sodium tert-butoxide at 35°C. The yield of over all reactions for the synthesis of p-chloromethylstyrene was 41%. This procedure is simpler and gives a higher yield than those [5-7] described previously; further, the materials used are readily available and are inexpensive.

p-Chloromethylstyrene obtained by this method was polymerized smoothly in the presence of AIBN at 60°C. Obtained polymer easily dissolved in benzene and dichloromethane.

TABLE 1. Results of the Radical Copolymerization of p-Chloromethylstyrene (Monomer I) with Styrene Initiated by AIBN at 60° C[a]

[I] (mmole)	[Styrene] (mmole)	Time (hr)	Conversion (%)	Copolymer composition Cl (%)	Copolymer composition [I] (mole %)
5.1	44.6	2	3.6	4.63	14.5
10.1	39.9	2	3.2	7.61	24.9
15.0	34.9	2	2.8	11.19	38.8
22.0	30.1	2	3.5	13.09	46.8
24.9	25.0	2	2.7	15.47	58.9
30.3	19.9	2	3.2	17.36	68.0
34.8	15.3	2	4.7	19.15	76.1
39.8	10.5	2	5.7	19.95	80.6
44.9	5.5	2	6.4	21.53	89.5

[a] [AIBN] = 5 × 10^{-3} mole/liter; benzene, 5 ml.

TABLE 2. Results of the Radical Copolymerization of 4-Chloromethylstyrene (I) with Methyl Methacrylate Initiated by AIBN at 60° C[a]

[I] (mmole)	[Methyl methacrylate] (mmole)	Time (min)	Conversion (%)	Copolymer composition Cl (%)	Copolymer composition [I] (mole %]
5.1	45.3	120	4.1	6.50	20.3
10.2	40.3	120	3.6	9.98	32.9
15.1	35.6	140	2.6	12.12	41.6
20.2	30.2	140	2.3	13.20	46.3
25.0	25.5	150	1.5	15.45	56.5
29.7	19.8	150	1.7	16.86	63.4
34.3	15.3	180	1.8	18.56	72.2
39.2	10.6	180	1.6	19.66	78.2
45.1	5.2	180	1.3	21.87	91.2

[a] [AIBN] = 5 × 10^{-3} mole/liter; benzene, 5 ml.

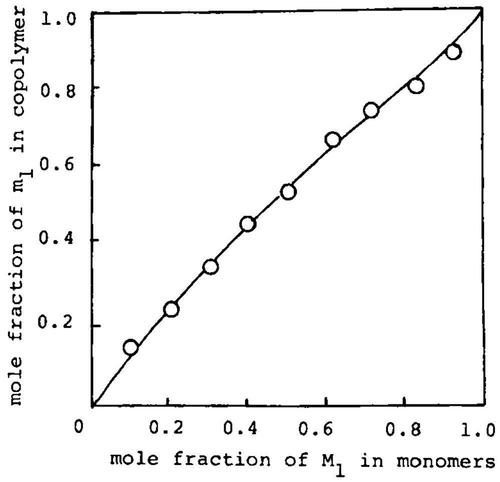


FIG. 2. Monomer-copolymer composition curve of p-chloromethylstyrene (M_1) and styrene (M_2).

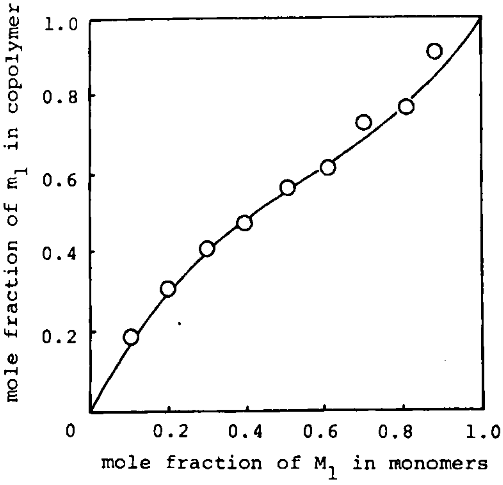


FIG. 3. Monomer-copolymer composition curve of p-chloromethylstyrene (M_1) and methyl methacrylate (M_2).

TABLE 3. Copolymerization Parameters of p-Chloromethylstyrene (I)

M_1	M_2	r_1	r_2	Q_1	e_1
I	Styrene	1.31	0.72	1.16	-0.58
I	Methyl methacrylate	0.82	0.37	1.13[a]	-0.69[a]
Styrene	Methyl methacrylate	0.52	0.46	1.0	-0.8

[a] Calculated from the values of Q = 0.74, e = 0.40 for methyl methacrylate.

Radical Copolymerization of p-Chloromethylstyrene with Styrene and Methyl Methacrylate

The results of radical copolymerizations of p-chloromethylstyrene with styrene and methyl methacrylate at 60°C are shown in Tables 1 and 2. The composition of the copolymers were calculated from their chlorine content. Figures 2 and 3 show the monomer-copolymer composition curves. Analyses of the copolymerization data for the p-chloromethylstyrene (M_1)-Styrene (M_2) system according to the Fineman-Ross method gave values of $r_1 = 1.32$, $r_2 = 0.72$. From these values of the monomer reactivity ratio for this system, the values of the resonance stabilization factor, Q_1 and electrical factor, e_1 were calculated by the equation of Alfrey and Price [10]. The values $Q_1 = 1.16$, $e_1 = 0.58$ were obtained by using the values $Q_2 = 1.0$, $e_2 = -0.8$ for styrene. Radical copolymerization parameters of p-chloromethylstyrene with methyl methacrylate as comonomer was also studied. The results are summarized in Table 3.

As can be seen from Table 3, Q and e values which are obtained from the copolymerization with styrene and methyl methacrylate are in good agreement within experimental error. The e value for p-chloromethylstyrene is somewhat larger than that of styrene; the chloromethyl group is classified as electron-withdrawing group. The values for the free-radical stabilization factor, Q for this compound is quite comparable to that of styrene, but slightly larger. This result seems to reflect the hyperconjugation of chloromethyl group [11]. From the results of copolymerization of p-chloromethylstyrene, it was found that the character of p-chloromethylstyrene resembles that of styrene.

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