Copolymerization of New Styrene Derivatives Having Alkylamino Group: *p*-Diethylaminoethylstyrene, *m*-Diethylaminoethylstyrene and a Quaternized Derivative

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ABSTRACT: The copolymerization behavior of new styrene derivatives, namely, *p*-diethylaminoethylstyrene (*p*-EAS), *m*-diethylaminoethylstyrene (*m*-EAS), and *p*-vinylphenethyltriethylammonium bromide (*p*-VPAB), was examined. Copolymerization parameters of *m*-EAS were similar to those of styrene or *m*-methylstyrene, and a significant effect of the diethylaminoethyl group was observed in *p*-EAS. *Q*, *e*-Values of *p*-EAS were very close to those of *p*-dimethylaminostyrene. When *p*-EAS was copolymerized with acrylamide (AAM) in methanol, *p*-EAS exhibited a greater reactivity than AAM, which may be explained as a possible effect of the *p*-EAS causing an increase in the equilibrated concentration of the less reactive isomeric form of AAM. In the copolymerization of cationic monomer, *p*-VPAB, with MMA, *p*-VPAB exhibited less reactivity than MMA, owing to Coulombic repulsion between *p*-VPAB and the growing chain-end.

KEY WORDS Copolymerization / New Monomers / *p*-Diethylaminoethylstyrene / *m*-Diethylaminoethylstyrene / *p*-Vinylphenethyltriethylammonium Bromide / Monomer Reactivity Ratios / *Q*, *e*-Values / Polyamines / Polycations / Functional Polymers /

As reported in a previous paper,¹ the reaction of *p*-divinylbenzene (*p*-DVB) and diethylamine catalyzed by lithium diethylamide gave *p*-diethylamino-

ethylstyrene (*p*-EAS) or 1,4-bis(2-diethylaminoethyl)benzene (*p*-BEAB), selectively and quantitatively (see eq 1 and 2).

Similarly, *m*-diethylaminoethylstyrene and 1,3-bis(2-diethylaminoethyl)benzene (*m*-BEAB) were selectively synthesized from *m*-divinylbenzene.²

New polymers having alkylamino- or alkylammonio-substituents can be derived from EAS or

its quaternized derivative as starting monomers. These polymers have properties expected to hold promise for biomedical³⁻⁷ or environmental⁸ applications.

In this study, the copolymerization behavior of *p*-EAS, *m*-EAS, and *p*-vinylphenethyltriethylammonium bromide (*p*-VPAS) was examined to obtain information useful for synthesizing a variety of copolymers having alkylamino groups.

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EXPERIMENTAL

Materials

The solvents were purified by conventional methods. Styrene was successively washed with an aqueous solution of sodium thiosulfate, dilute aqueous solution of sodium hydroxide, and water; it was then dried over barium oxide, and distilled twice under reduced pressure. Methyl methacrylate (MMA) and ethyl acrylate were successively washed with a dilute aqueous solution of sodium sulfite, 5% aqueous solution of sodium hydroxide, and 2% aqueous solution of sodium chloride; they were dried over sodium sulfate, and distilled twice under reduced pressure. Acrylamide (AAM) was recrystallized from benzene, and dried *in vacuo* at room temperature. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol and dried *in vacuo* at room temperature. Preparation of *p*-EAS, *m*-EAS, and *p*-VPAB was reported previously.^{1,2,4}

nitrogen, was charged with monomers, solvent, and initiator. The ampoule was sealed *in vacuo*. Polymerization was carried out at 60°C. The copolymer was precipitated twice by a large excess of a non-solvent, and dried *in vacuo* at room temperature until a constant weight was reached. The freeze-drying technique was also adopted in a certain series of experiments.

Determination of Copolymer Composition

Copolymer compositions were determined by analysis for nitrogen contents. In a certain series of experiments, ¹H NMR spectroscopy was also used for the determination of copolymer composition by comparison of the integral intensity of aliphatic and aromatic hydrogens. The Kelen-Tüdös method was used for the calculation of monomer reactivity ratios.⁹

RESULTS

Copolymerization Procedure

A glass ampoule, which had been flushed with dry

Determination of Monomer Reactivity Ratios

The copolymerization results are listed in Tables

Table I. Copolymerization of *p*-diethylaminoethylstyrene (*p*-EAS) (M_1) with MMA (M_2) in toluene at 60°C^a

Run no.	Amount of monomer feed		mol% of M_1 in monomer feed	Yield ^b /%	N/%	mol% of M_1 in polymer
	M_1 /mmol	M_2 /mmol				
1	1.90	8.02	19.2	2.0	3.39	32.3
2	4.18	6.23	40.2	11.4	4.28	44.7
3	5.58	7.29	44.5	12.6	4.31	45.1
4	6.47	4.15	60.9	8.7	4.60	49.7

^a Toluene, 2 cm³; AIBN, 0.02 mmol; polymerization time, 2 h.

^b Petroleum ether-insoluble fraction at -50°C.

Table II. Copolymerization of *p*-EAS (M_1) with styrene (M_2) in toluene at 60°C^a

Run no.	Amount of monomer feed		mol% of M_1 in monomer feed	Yield ^b /%	N/%	mol% of M_1 ^c in polymer
	M_1 /mmol	M_2 /mmol				
1	1.83	8.24	18.2	6.27	1.67	14.1 (17.0)
2	3.31	6.72	33.0	3.47	2.82	26.2 (28.8)
3	4.24	6.32	40.2	4.01	3.41	33.4 (36.3)
4	4.68	5.14	47.8	4.92	4.06	42.4 (44.5)
5	7.80	2.26	77.5	6.46	5.52	67.4 (70.8)

^a Toluene, 3 cm³; AIBN, 0.02 mmol. Polymerization time: run 1, 2, and 3, 150 min; run 4, 240 min; run 5, 270 min.

^b Petroleum ether-insoluble fraction at -50°C.

^c Values designated in parentheses were evaluated from the ¹H NMR spectra of the copolymers.

Copolymerization of New Monomers Having Amino Group

Table III. Copolymerization of *p*-EAS (M_1) with AAm (M_2) in methanol at 60°C^a

Run no.	Amount of monomer feed		mol% of M_1 in monomer feed	Yield ^b /%	N/%	mol% of M_1 in polymer
	M_1 /mmol	M_2 /mmol				
1	0.93	8.99	9.4	3.53	11.85	35.5
2	1.81	8.21	18.1	11.6	9.93	53.0
3	2.98	7.04	29.7	4.40	9.28	60.3
4	4.29	5.93	42.0	9.19	8.48	71.3
5	6.40	4.14	60.7	4.11	7.53	86.9

^a Methanol, 2 cm³: AIBN, 0.02 mmol; Polymerization time: run 1 and 3, 60 min; run 2, 90 min; run 4 and 5, 110 min.^b Acetone-insoluble fraction at -50°C.**Table IV.** Copolymerization of *p*-vinylphenethyltriethylammonium bromide (*p*-VPAB) (M_1) with MMA (M_2) in methanol at 60°C^a

Run no.	Amount of monomer feed		mol% of M_1 in monomer feed	Yield ^b /%	mol% of M_1 in polymer
	M_1 /mmol	M_2 /mmol			
1	2.72	6.72	28.8	10.33	23.4
2	4.73	4.65	50.4	6.64	38.8
3	5.15	3.72	58.1	6.23	41.9
4	7.13	2.51	74.0	3.49	50.8

^a Methanol, 3 cm³: AIBN, 0.02 mmol; polymerization time, 3 h.^b Acetone-insoluble fraction at -50°C.^c Determined by means of ¹H NMR spectroscopy.**Table V.** Copolymerization of *m*-diethylaminoethylstyrene (*m*-EAS) (M_1) with MMA (M_2) in toluene at 60°C^a

Run no.	Amount of monomer feed		mol% of M_1 in monomer feed	Yield ^b /%	N/%	mol% of M_1 in polymer
	M_1 /mmol	M_2 /mmol				
1	1.87	8.23	18.5	2.76	2.94	26.8
2	6.07	8.30	42.0	1.50	4.17	42.9
3	5.49	5.71	49.0	16.60	4.52	48.3
4	5.39	5.09	51.0	7.51	4.54	49.0
5	6.27	3.98	61.2	5.29	5.02	57.0
6	6.18	3.76	62.0	22.40	5.02	57.0
7	7.96	2.75	74.3	2.59	5.55	67.2

^a Toluene, 3 cm³: AIBN, 0.02 mmol. Polymerization time: run 1, 2, and 4, 240 min; run 3 and 6, 360 min; run 5 and 7, 180 min.^b Petroleum ether-insoluble fraction at -50°C.

I—VII.

As shown in Table VIII, the monomer reactivity ratios were calculated from the data listed in Tables I—VII by the method of Kelen and Tüdös.⁹

In Table IX are listed the Alfrey-Price *Q*- and *e*-values for EAS and VPAB calculated from the monomer reactivity ratios.

Table VI. Copolymerization of *m*-EAS (M_1) with styrene (M_2) in toluene at 60°C^a

Run no.	Amount of monomer feed		mol% of M_1 in monomer feed	Yield ^b /%	mol% of M_1 ^c in polymer
	M_1 /mmol	M_2 /mmol			
1	2.04	7.95	20.4	2.97	20.2
2	2.80	6.87	29.0	6.42	26.5
3	4.01	6.02	40.0	3.70	38.4
4	4.84	5.29	47.8	2.06	48.4
5	5.75	3.82	60.1	4.23	57.0
6	9.61	4.43	68.4	8.45	69.9
7	7.67	2.83	73.0	5.10	75.4
8	9.20	2.17	80.9	4.83	84.2

^a Toluene, 3 cm³ (run 6, 4.5 cm³); AIBN, 0.02 mmol (run 6, 0.03 mmol); polymerization time, 180 min.^b Petroleum ether-insoluble fraction at -50°C.^c Determined by ¹H NMR spectroscopy.**Table VII.** Copolymerization of *m*-EAS (M_1) with ethyl acrylate (M_2) in toluene at 60°C^a

Run no.	Amount of monomer feed		mol% of M_1 in monomer feed	Yield ^b /%	N/%	mol% of M_1 in polymer
	M_1 /mmol	M_2 /mmol				
1	3.87	15.88	19.6	4.3	3.68	36.1
2	6.17	13.56	31.3	3.6	4.41	46.7
3	8.09	11.06	42.4	3.6	4.71	51.6
4	10.59	9.27	53.3	5.6	5.11	58.6
5	12.56	7.67	62.1	4.7	5.18	59.9
6	13.71	5.61	71.0	2.6	5.56	67.4

^a Toluene, 6 cm³; AIBN, 0.04 mmol; polymerization time, 60 min.^b Petroleum ether-insoluble fraction at -50°C.

DISCUSSION

Comparison of Copolymerization Parameters for *p*-EAS, *m*-EAS and Other Related Styrene Derivatives

As seen in Tables VIII and IX, *p*-EAS has a larger *Q*-value and a more negative *e*-value than styrene and *p*-methylstyrene.

It is well known that *e*-values are correlated linearly with Hammett's σ -values of substituents.¹⁵ Though the σ -value of the diethylaminoethyl group ($\sigma_p = -0.14$)¹ is almost equal to that of the methyl group ($\sigma_p = -0.17$),¹⁶ copolymerization parameters for *p*-EAS and *p*-methylstyrene are markedly different from each other. Surprisingly, the *Q* and *e*-values for *p*-EAS are rather close to that of *p*-dimethylaminostyrene, which possesses a dimethylamino group ($\sigma_p = -0.44$)¹⁶ directly at the *para*-

position of the aromatic ring.

Since a fairly small $r_1 r_2$ value ($r_1 r_2 = 0.03$) was obtained in the copolymerization of *p*-EAS with MMA, the alternating nature of copolymer obtained was higher than that of copolymers of styrene with MMA ($r_1 r_2 = 0.24$).

In contrast with *p*-EAS, the copolymerization behavior of *m*-EAS is nearly the same as that of *m*-methylstyrene.

Copolymerization of *p*-EAS with Acrylamide (*A*Am)

In the copolymerization of *p*-EAS with *A*Am, *p*-EAS exhibited an unexpectedly greater reactivity than *A*Am, and the copolymer formed was richer in *p*-EAS units than in the monomer mixture (see Table III). This may be explained if the possibility of an interaction between *A*Am and *p*-EAS is assumed. The diethylaminoethyl group, a weak base, in *p*-

Table VIII. Monomer reactivity ratios

M ₁	M ₂	r ₁	r ₂	r ₁ r ₂	Solvent	Temp/°C	ref
<i>p</i> -EAS	MMA	0.11	0.26	0.03	Toluene	60	This work
"	Styrene	0.59	1.24	0.73	"	"	"
"	AAm	3.35	0.15	0.50	Methanol	"	"
<i>m</i> -EAS	MMA	0.46	0.53	0.24	Toluene	60	This work
"	Styrene	1.0	1.0	1.0	"	"	"
"	Ethyl acrylate	0.49	0.21	0.10	"	"	"
<i>p</i> -VPAB	MMA	0.15	0.95	0.14	Methanol	60	This work
Styrene	MMA	0.52	0.46	0.24	Bulk	60	10
"	AAm	1.44	0.30	0.43	Ethanol	70	11
"	"	1.27	1.38	1.75	Dioxane	"	"
<i>p</i> -Methylstyrene	MMA	0.44	0.405	0.18	Bulk	60	12
<i>m</i> -Methylstyrene	MMA	0.49	0.53	0.26	Bulk	60	12
<i>p</i> -Dimethylaminostyrene	MMA	0.11	0.205	0.02	Bulk	60	12
	Styrene	0.84	1.015	0.85	"	"	"

Table IX. *Q*- and *e*-values^a

Monomer (1)	Monomer (2) ^b	<i>Q</i> ₁	<i>e</i> ₁
<i>p</i> -EAS	MMA	1.32	-1.48
"	Styrene	1.26	-1.36
<i>m</i> -EAS	MMA	0.85	-0.78
"	Styrene	1.0	-0.8
"	Ethyl acrylate	0.79	-0.89
<i>p</i> -VPAB	MMA	0.45	-0.99
<i>p</i> -Methylstyrene	MMA	1.08	-0.91
<i>m</i> -Methylstyrene	MMA	0.88	-0.76
<i>p</i> -Dimethylamino- styrene	MMA	1.65	-1.55
	Styrene	1.36	-1.20

^a *Q*- and *e*-values were calculated from the data cited in Table VIII.

^b Styrene (*Q*=1.0, *e*=-0.8).¹³ MMA (*Q*=0.74, *e*=0.40).¹³ Ethyl acrylate (*Q*=0.42, *e*=0.62).¹⁴

EAS, may affect the following equilibria by a shift to the right eq 3.

The enolate form of AAm is known to be less reactive than the keto form isomer.¹¹

Copolymerization Behaviors of *p*-Vinyl-phenethyltriethylammonium Bromide (*p*-VPAB)

As can be seen from Table VIII, *p*-VPAB is less reactive than MMA, and the copolymer formed is poorer in *p*-VPAB units than in the monomer mixture. It is considered that Coulombic repulsion between *p*-VPAB and polymer chain may interfere with the approach of the charged monomer to the growing chain-end.

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