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Lithium Alkylamide Catalyzed Addition Reaction of Alkylamine to Vinyl Monomers. II. Preparation and *Q*,*e*-Values of New Styrene Derivative: (*S*)-*N*-α-Methylbenzyl-3-vinylphenethylamine

Hiroshi HAMANA,* Koichi HORIGUCHI, Tokio HAGIWARA, and Tadashi NARITA
Department of Enviromental Engineering, Saitama Institute of Technology, Okabe-machi, Osato-gun, Saitama 369-02

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The lithium alkylamide catalyzed addition reaction of α-methylbenzylamine with 1,3-divinylbenzene (*m*-DVB) was found to produce *N*-α-methylbenzyl-3-vinylphenethylamine (1:1 adduct) (*m*-MBVPA), which is a new styrene derivative, and 1,3-bis(*N*-α-phenethyl-2-aminoethyl)benzene (1:2 adduct). The specific rotation of (*S*)-*N*-α-methylbenzyl-3-vinylphenethylamine derived from the optically active (*S*)-α-methylbenzylamine with *m*-DVB was found to be $[\alpha]_D^6=-62.2°$ (*c* 1.46, CH_3OH). The higher reactivity of 1,4-divinylbenzene (*p*-DVB) compared to *m*-DVB in this addition reaction system is ascribable to a larger conjugation of *p*-DVB. The vinyl group of *m*-MBVPA has been found to show a higher reactivity compared to that in the adduct of MBA with *p*-DVB. The monomer reactivity ratios and *Q*,*e*-values obtained from the radical copolymerization of *m*-MBVPA (M_1) and styrene (M_2) were $r_1=0.48$, $r_2=0.70$; $Q_1=0.62$, and $e_1=0.24$.

The lithium diethylamide catalyzed addition reaction of diethylamine to butadiene has been reported to selectively form *cis*-1-diethylamino-2-butene in high yields.[1)] The investigation on the reaction system of dialkylamine and 1,3- and 1,4-divinylbenzenes has also opened a new route to styrene derivatives possessing alkylamino groups,[2—4)] and to their polymerization products for which some applications have been developed.

In a previous report we described how a styrene derivative having an optically active group was synthesized from 1,4-divinylbenzene (*p*-DVB) and (*S*)-α-methylbenzylamine ((*S*)-MBA) catalyzed with lithium (*S*)-α-methylbenzylamide.[5)] This might provide a new reaction which yields an optically active adducts of conjugated dienes, with the amines possessing phenyl or benzyl moieties.

In order to examine this reaction in greater detail, the reactions of 1,3-divinylbenzene (*m*-DVB) with α-methylbenzylamine (MBA) and (*S*)-MBA were investigated with respect to the synthesis of a new styrene derivative possessing an optically active group. Further development in comparison to the reactivity between *m*-DVB and *p*-DVB with MBA is also described. The polymerization reactivity of the new monomer, thus synthesized, such as *Q*,*e*-values, is presented.

Experimental

Most of the experiments, such as distillation and anionic addition reaction, were carried out under a purified nitrogen atmosphere in order to preclude oxygen and moisture.

Reagents. Commercial (*RS*)-α-methylbenzylamine (MBA) was purified by refluxing over calcium hydride and then distilling under reduced pressure. 1,3-Divinylbenzene (*m*-DVB) and 1,4-divinylbenzene (*p*-DVB) (supplied by Asahi Chemical Industry Co.) was refluxed over calcium hydride and then distilled under reduced pressure. (*S*)-α-Methylbenzylamine ((*S*)-MBA) ($[\alpha]_D^5=-40.9°$ (neat)) was prepared by resolution of racemate with (+)-tartaric acid.[6)] Commercial butyllithium was used after determining the concentration of the hexane solution by a double titration method.[7)] Other reagents and solvents were purified by conventional methods.

***N*-α-Methylbenzyl-3-vinylphenethylamine (*m*-MBVPA).** To a toluene (30 ml) solution of MBA (50 mmol), 1 mmol of butyllithium was added in order to synthesize a catalytic amount of the lithium amide at room temperature. Then, 50 mmol of *m*-DVB was introduced into the solution. After the reaction mixture was kept at 40 °C for 5 days, a small amount of methanol was added in order to stop the reaction. The product was isolated by fractional distillation, giving 23.3 g (37%); bp 135.5 °C (4Pa). ^1H NMR ($CDCl_3$, 60 MHz) δ=1.25—1.36 (4H, d, *J*=7 Hz, CH_3 and NH), 2.75 (4H, s, CH_2), 3.63—3.92 (1H, q, *J*=6 Hz, $C\underline{H}CH_3$), 5.08—5.83 (2H, dd, *J*=13, 17 Hz, $C=CH_2$), 6.45—6.93 (1H, dd, *J*=10, 19 Hz, CH=C), 7.20—7.26 (9H, C_6H_4 and C_6H_5). Found: C, 86.14; H, 8.29; N, 5.57%. Calcd for $C_{18}H_{21}N$: C, 86.01; H, 8.42; N, 5.57%.

(*S*)-*N*-α-Methylbenzyl-3-vinylphenethylamine ((*S*)-*m*-MBVPA). The reaction of *m*-DVB with (*S*)-MBA was carried out by the same method, giving 1.2 g (9.2%). $[\alpha]_D^6=-62.2°$ (*c* 1.46, CH_3OH).

1,3-Bis[2-(1-phenethylamino)ethyl]benzene (*m*-BPAB). To a toluene (15 ml) solution of MBA (240 mmol), 5 mmol of butyllithium was added in order to synthesize a catalytic amount of the lithium amide. 30 mmol of *m*-DVB was added into the solution. After the reaction mixture was kept at 50 °C for 6 days, a small amount of methanol was added in order to stop the reaction. The product was isolated by fractional distillation giving 6.9 g (62%); bp 220 °C (4pa). MS (70 eV) *m*/*z* (rel intensity) 373 ($M+1^+$; 7), 239 (100), 135 (11), 134 (13), and 105 (64). ^1H NMR ($CDCl_3$, 60 MHz) δ=1.25—1.36 (8H, d, *J*=7 Hz, CH_3 and NH), 2.72 (8H, s, CH_2), 3.59—3.91 (2H, q, *J*=5 Hz, $C\underline{H}CH_3$), 7.02 (4H, m, C_6H_4), 7.27 (10H, s, C_6H_5). Found: C, 83.24; H, 8.67; N, 7.23%. Calcd for $C_{26}H_{32}N_2$: C, 83.82; H, 8.66; N, 7.52%.

Dependence of Product Yield on the Reaction Time. An equimolar reaction of MBA with *m*-DVB was carried out in toluene catalyzed by lithium alkyl amide, as described above. The reaction temperature was thermostated at 40±0.2 °C. The reaction was quenched after appropriate time intervals by sampling portions of the reaction mixture and adding them to methanol. The concentrations of the starting materials and products were determined by vapor-phase chromatography using pentadecane as an internal standard.

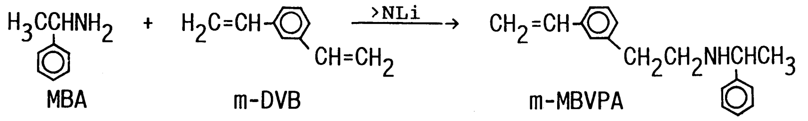
Radical Copolymerization. Styrene, *m*-MBVPA (totally 20 mmol), benzene (1 ml) and 2,2′-azobisisobutyronitrile (0.01 mmol) were introduced into a glass ampoule. A copolymerization reaction was then carried out at 70 °C. The polymer was isolated by precipitation with petroleum ether and drying to constant weight. The copolymer composition was determined by elemental analysis.

Measurements. Vapor-phase chromatography was measured by a HEWLETT PACKARD 5890A equipped with FID. Column: Fused silica 5 m×0.53 mm, methyl silicone gum. The column temperature was programmed 100—300 °C at 20 °C min^{-1}. The ^{1}H NMR spectrum was measured with a Hitachi R-600 FT-NMR and the ^{13}C NMR spectrum with a JEOL GSX-270 FT-NMR. The molecular weights of reaction products were measured with a JEOL-QH100 GC-MS. The D-line specific rotation was measured with a JASCO DIP-4 digital polarimeter.

Results and Discussion

Two new peaks (product (I) and product (II)) in addition to *m*-DVB, MBA, the solvent and the internal standard appeared in the vapor-phase chromatogram 6 h after the reaction started. The peaks of product (I) and (II) gradually increased with the reaction time.

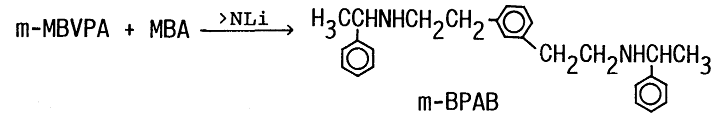
Product (I) was isolated by distillation, as described in the experimental part. The ^{1}H NMR and the elemental analysis of product (I) suggest the structure of *m*-MBVPA in Eq. (1).



(1)

Based on the results of racemic MBA with *m*-DVB, an examination of the reaction between the optically active (*S*)-MBA and *m*-DVB successfully showed a new styrene derivative, (*S*)-*m*-MBVPA, possessing an optically active amine moiety. The yield was rather low, as described in the experimental section. This compound might be a promising monomer to form various optically active polymers.

The mass spectrum and the retention time of the reaction product (II) agreed with those of *m*-BPAB, which was synthesized under other reaction conditions, as described in the experimental part. The mass spectrum, elemental analysis, and ^{1}H NMR of *m*-BPAB suggest a 1:2 addition product, as descrived in Eq. 2.



(2)

Table 1. Time Dependence of the Reaction of (*RS*)-α-Methylbenzylamine (MBA) with 1,3-Divinylbenzene (*m*-DVB)[a)]

Time h	[MBA] mmol	[*m*-DVB] mmol	[*m*-MBVPA] mmol	[*m*-BPAB][b)] mmol	[*m*-DVB]+[*m*-MBVPA]+[*m*-BPAB][c)] mmol
3	0.70	0.70	0.21	0	0.91
6	0.62	0.64	0.32	0.02	0.98
9	0.53	0.57	0.38	0.04	0.99
12	0.48	0.52	0.41	0.04	0.97
15	0.43	0.48	0.44	0.05	0.97
18	0.41	0.46	0.46	0.05	0.97
24	0.36	0.42	0.50	0.06	0.98
36	0.27	0.34	0.51	0.07	0.92
48	0.24	0.33	0.56	0.09	0.98
60	0.21	0.31	0.54	0.10	0.95
72	0.20	0.30	0.55	0.10	0.95
84	0.18	0.28	0.56	0.10	0.94
96	0.15	0.26	0.58	0.11	0.94
108	0.15	0.26	0.57	0.11	0.94
121	0.14	0.25	0.58	0.11	0.94

a) [*m*-DVB]$_0$=0.97 mol dm^{-3}. b) [*m*-BPAB]=[*m*-DVB]−[MBA]. c) [*m*-DVB]+[*m*-MBVPA]+[*m*-BPAB] should be equal to the initial concentration of [*m*-DVB]$_0$.

In order to compare the reactivity between *m*-DVB and *p*-DVB under the same reaction conditions, the time dependence of the concentrations of MBA, *m*-DVB and *m*-MBVPA in the reaction mixtures are shown in Fig. 1(A) and Table 1. Preliminary information concerning the reactivity of *p*-DVB with MBA and the data of Fig. 1(B) were presented in a previous paper.[5] The concentrations of MBA and *m*-DVB (Fig. 1(A)) were found to decrease more slowly at an early stage of the reaction compared to those of MBA and *p*-DVB in Fig. 1(B), which evidently shows that the reactivity of *m*-DVB is lower than that of *p*-DVB during first-step addition reactions (Eq. 1). Although the concentrations of the second-step addition products could not be measured because of the high boiling temperature, the formation of these compounds should be proportional to the differences between the concentrations of *m*-DVB and MBA ([*m*-BPAB]=[*m*-DVB]=[MBA]). The initial concentration of *m*-DVB, [*m*-DVB]$_0$ should be equal to [*m*-DVB]+[*m*-MBVPA]+[*m*-BPAB]. As shown in the last column of Table 1, the obtained values satisfactorily agree with the initial concentration of *m*-DVB ([*m*-DVB]$_0$=0.97 mol dm^{-3}) within the experimental error. Therefore, no remarkable side reactions, such as polymerization of *m*-DVB, takes place.

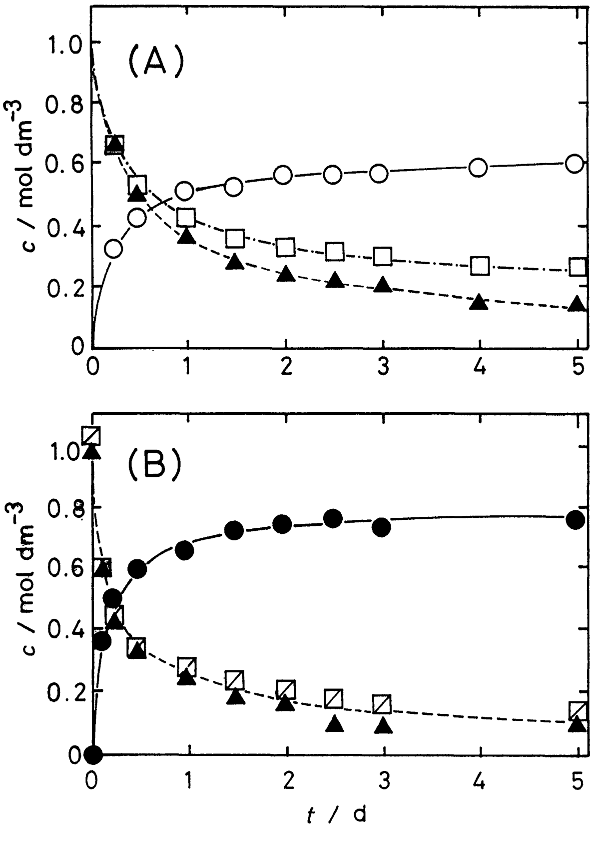


Fig. 1. Time dependence of the reaction of MBA with *m*-DVB (A) and MBA with *p*-DVB (B), *m*-MBVPA (○), *m*-DVB (□), MBA (▲), *p*-MBVPA (●), *p*-DVB (□); Reaction conditions: [*m*-DVB]$_0$=[*p*-DVB]$_0$=0.97 mol dm^{-3}, [MBA]$_0$=0.95 mol dm^{-3}, [>NLi]=0.02 mol dm^{-3} in toluene at 40 °C.

The reaction of MBA with *m*-DVB during first-step addition (Eq. 1) was found to be slower compared to the reaction of MBA with *p*-DVB, as mentioned above. The reactions of diethylamine with *m*-DVB and *p*-DVB have been reported to show similar results.[8] The higher reactivity of *p*-DVB may be ascribed to a 10-membered conjugation system, compared to the 8-membered conjugation of *m*-DVB.

The reactivity of the vinyl group in *m*-MBVPA is, on the contrary, higher compared to that in the reaction product (*p*-MBVPA) of MBA with *p*-DVB since the ([*m*-DVB]−[MBA]) values are larger than those for *p*-DVB (Fig. 1). These phenomena may be related to the electron density of the vinyl groups since the reactions are apparently anionic, as reported in the reaction system of diethylamine with *m*-DVB and *p*-DVB,[9] in order to obtain information concerning the electron density, ^{13}C NMR chemical shifts of β-carbons of these monomers including divinylbenzenes were measured (summarized in Table 2). The δ values of the β-carbons were found to be in the order styrene>*m*-MBVPA>*p*-MBVPA. The reactivity of *m*-MBVPA and *p*-MBVPA may, therefore, be governed by the electron density of the β-carbon of the vinyl group.

The *e*-value of Alfrey–Price's *Q*,*e*-scheme is one of the most important scales for estimating the effect of the substituents on the reactivity of vinyl monomers. The results of a radical copolymerization of *m*-MBVPA (M_1) with styrene (M_2) are summarized in Table 3 and Fig. 2. The monomer reactivity ratios calculated from the data in Table 2 by the Kelen–Tüdős method[10] are r_1=0.48 and r_2=0.70. From the monomer reactivity ratios, *Q*,*e*-values of *m*-MBVPA were calculated to be Q_1=0.62 and e_1=0.24. Regarding the radical copolymerization of para isomer (M_1) and styrene (M_2), Q_1=1.59 and e_1=−1.28.[5] The higher electron density of the β-carbon of *m*-MBVPA, as mentioned above, has been confirmed, since the *e*-value of *m*-MBVPA was found to be larger than that of *p*-MBVPA. Yukawa et al. have also reported a similar tendency regarding the styrene derivatives, such as *m*-[2-(diethylamino)ethyl]-styrene (*Q*=1.0, *e*=−0.8) and *p*-[2-(diethylamino)ethyl]-styrene (*Q*=1.26, *e*=−1.36).[11]

Table 2. ^{13}C NMR Chemical Shift of the β-Carbon of Styrene Derivatives in $CDCl_3$ Solution

Styrene derivative	δ from TMS ppm	Δδ[a)] ppm
m-MBVPA	113.73	−0.02
p-MBVPA	113.09	−0.66
1,3-Divinylbenzene (*m*-DVB)	114.04	0.29
1,4-Divinylbenzene (*p*-DVB)	113.72	−0.03
Styrene	113.75	0

a) Δδ=δ (styrene derivative)−δ (styrene).

Table 3. Copolymerization of *m*-MBVPA(M_1) with Styrene(M_2) in Benzene at 70 °C

Run No.	Ammount of monomer feed		mol% of M_1 in monomer feed	Yield	N	mol% of M_1 in polymer
	M_1/mmol	M_2/mmol		%	%	
1	3.0	17.0	15	15.4	1.89	17.5
2	7.0	13.0	35	10.3	2.99	35.1
3	10.0	10.0	50	16.3	3.70	46.8
4	13.0	7.0	65	14.0	4.34	59.9
5	17.0	3.0	85	7.1	4.41	75.5

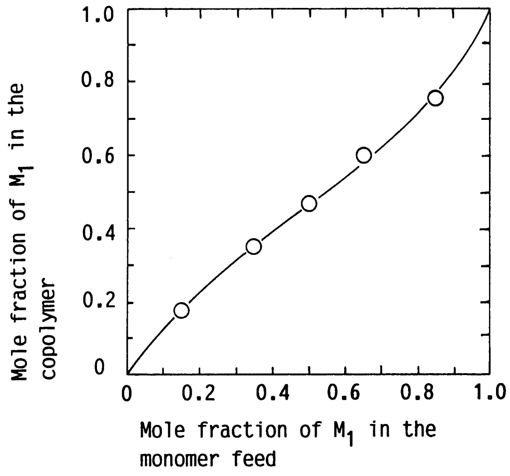


Fig. 2. Copolymer composition curve for system of *m*-MBVPA (M_1) and styrene (M_2).

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