Synthesis and Free-Radical Polymerization of Triazinylstyrene Derivatives

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ABSTRACT

Reaction of 2,4-dichloro-6-p-vinylphenyl-1,3,5-triazine with nucleophilic reagents such as diethylamine, ethanol, diethyleneglycol monomethylether, and ethanthiol in the presence of a base in THF gave the corresponding substituted compounds in moderate to high yields. The resulting monomers, which have two functional groups, polymerized readily in the presence of AIBN at 60°C to afford the corresponding homopolymers. The copolymerization parameters of each monomer were calculated from their copolymerization with styrene. Q values of these monomers were larger than that of styrene, indicating participation of the triazine ring to resonance of the monomers. On the other hand, e values of these monomers were approximately zero because of the electron-withdrawing character of the triazinyl group.

INTRODUCTION

Polymer catalysts and reagents have been developed recently and are used extensively in organic synthesis [1–4]. This is mainly due to the easy separation of the product and reuse of the catalyst or regeneration of the spent reagent. These functional polymers have been prepared by anchoring active groups to polymer supports or polymerization of functional monomers. These polymers occasionally

show higher activity or reactivity than their corresponding monomeric compounds [5-10]. In most cases this polymer effect is caused by two factors, one is the formation of an attractive microenvironment around the active sites, and the other is a cooperative interaction of more than two functional groups.

The degree of cooperative interaction of functional groups would be increased with an increasing density of active sites. However, most functional polymers have only one functional group per monomer unit. Therefore, we recently prepared polymer supports having two replaceable groups, i.e., the dichlorotriazinyl moiety [11, 12]. Polymeric phase transfer catalysts prepared from these polymer supports showed higher activity [11, 13]. However, in polymer synthesis by polymer reaction, conversion of functional groups is often incomplete.

On the other hand, most functional monomers are styrene derivatives because of the ease of homopolymerization or copolymerization with styrene itself. These are generally prepared from chloromethylstyrene or bromostyrene.

There has been little work on the synthesis of functional monomers with two functional groups [14-17]. More recently, we reported the convenient synthesis of 2,4-dichloro-6-*p*-vinyl-1,3,5-triazine (**1**) which can be regarded as a reactive monomer containing two replaceable groups [12]. In this paper we describe the synthesis and free-radical polymerization of some monomers with two functional groups.

EXPERIMENTAL

Materials

2,4-Dichloro-6-*p*-vinylphenyl-1,3,5-triazine (**1**) was synthesized by the reaction of *p*-phenylvinylmagnesium chloride with cyanuric chloride [17]. Styrene and solvents were purified by distillation after appropriate drying. Azobisisobutyronitrile (AIBN) was recrystallized before use. Other reagents were obtained commercially and were used without further purification.

Synthesis of 2,4-Bis(diethylamino)-6-*p*-vinylphenyl-1,3,5-triazine (2)

A solution of diethylamine (1.82 g, 25 mmol) in THF (50 mL) was added slowly to a stirred solution of **1** (1.26 g, 5.0 mmol) in THF (50 mL) at 0°C. After stirring at room temperature for 20 hours, the resulting solid was filtered off, and the solvent was removed under reduced pressure to give a white solid. The solid was recrystallized with cyclohexane. The yield was 1.36 g (83%), mp 68°C.

IR (KBr): $\nu_{CH=CH_2} = 905, 990$ cm^{-1}.

NMR (in CDCl$_3$): $\delta = 1.22$ (t, 12H), 3.69 (q, 8H), 5.27 (d, 1H), 5.77 (d, 1H), 6.74 (dd, 1H), 7.40 (d, 2H), and 8.33 ppm (d, 2H).

Analysis. Calculated for C$_{10}$H$_{27}$N$_5$: C, 70.12; H, 8.36; N, 21.51%. Found: C, 69.95; H, 8.50; N, 21.24%.

Synthesis of 2,4-Diethoxy-6-*p*-vinylphenyl-1,3,5-triazine (3)

To a mixture of sodium hydride (~60%, oil suspension, 1.00 g, 25 mmol) and THF (50 mL), a solution of ethanol (0.88 g, 19 mmol) in THF (50 mL) was added slowly at 0°C and stirred for 30 minutes at room temperature. To the reaction

mixture a solution of 1 (1.52 g, 6.0 mmol) in THF (100 mL) was added at 0°C, and was allowed to react for 20 hours at room temperature. The reaction mixture was poured into water, extracted with methylene chloride, and dried over sodium sulfate. After evaporation of the solvent, the resulting solid was recrystallized with cyclohexane. The yield was 1.19 g (73%), mp 66°C.

IR (KBr): $\nu_{CH=CH_2}$ = 930, 990 cm^{-1}.

NMR (in CDCl$_3$): δ = 1.49 (t, 6H), 4.59 (q, 4H), 5.40 (d, 1H), 5.91 (d, 1H), 6.81 (dd, 1H), 7.54 (d, 2H), and 8.49 ppm (d, 2H).

Analysis. Calculated for C$_{15}$H$_{17}$N$_3$O$_2$: C, 66.40; H, 6.32; N, 15.49%. Found: C, 66.68; H, 6.54; N, 15.21%.

Synthesis of 2,4-Bis(1,4,7-trioxaoctyl)-6-p-vinylphenyl-1,3,5-triazine (4)

To a mixture of sodium hydride (~60%, oil suspension, 2.51 g, 62.8 mmol) and THF (250 mL), a solution of diethyleneglycol monomethylether (5.44 g, 45.3 mmol) in THF (50 mL) was added slowly and further stirred for 30 minutes. Then a solution of 1 (5.04 g, 20 mmol) in THF (100 mL) was added slowly to the mixture, and was allowed to react for a further 20 hours at room temperature. The reaction mixture was poured into water, extracted with methylene chloride, and dried over sodium sulfate. After evaporation of the solvent, the residue was separated with column chromatography (Wakogel C-200 eluent: n-hexane/acetone = 3/1) to give an oily compound. The yield was 4.75 g (56%).

IR (KBr): $\nu_{CH=CH_2}$ = 930, 990 cm^{-1}.

NMR (in CDCl$_3$): δ = 3.38 (s, 6H), 3.57 (m, 4H), 3.73 (t, 4H), 3.91 (t, 4H), 4.67 (t, 4H), 5.38 (d, 1H), 5.89 (d, 1H), 6.78 (dd, 1H), 7.50 (d, 2H), and 8.44 ppm (d, 2H).

Analysis. Calculated for C$_{21}$H$_{27}$N$_3$O$_6$: C, 60.13; H, 6.97; N, 10.02%. Found: C, 60.61; H, 6.26; N, 9.85%.

Synthesis of 2,4-Bis(ethylthio)-6-p-vinylphenyl-1,3,5-triazine (5)

To a mixture of sodium hydride (~60%, oil suspension, 0.49 g, 12.3 mmol) and THF (40 mL), a solution of ethylmercaptan (0.6 g, 10 mmol) and THF (40 mL) was added slowly at 0°C, and further stirred for 30 minutes at room temperature. Then, to the reaction mixture, a solution of 1 (0.75 g, 3 mmol) in THF (100 mL) was added slowly at 0°C, and was allowed to react for 20 hours at room temperature. The reaction mixture was poured into water, extracted with methylene chloride, and dried over sodium sulfate. After evaporation of the solvent, the resulting residue was separated with column chromatography (Wakogel C-200, eluent: n-hexane/benzene = 2/1) to give a solid. The yield was 0.45 g (49%), mp 52°C.

IR (KBr): $\nu_{CH=CH_2}$ = 920, 990 cm^{-1}.

NMR (in CDCl$_3$): δ = 1.45 (t, 6H), 3.22 (q, 4H), 5.40 (d, 1H), 5.90 (d, 1H), 6.79 (dd, 1H), 7.53 (d, 2H), and 8.44 ppm (d, 2H).

Analysis. Calculated for C$_{15}$H$_{17}$N$_3$S$_2$: C, 59.37; H, 5.65; N, 13.85%. Found: C, 60.08; H, 5.97; N, 13.19%.
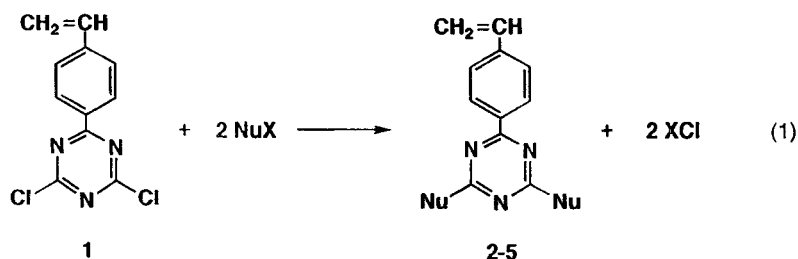
Polymerization

Polymerization was carried out in a sealed tube at 60°C. Charging of the reagents into an ampule and sealing of the ampule were done according to a method reported previously [18]. The tube was opened after polymerization, and its contents were poured into a large amount of methanol to precipitate the polymer. The resulting polymer was purified by reprecipitation from chloroform with ether. The copolymer composition was evaluated from the elementary analysis of carbon and nitrogen.

Measurements

IR spectra were measured by a Hitachi R-285 spectrometer. NMR spectra were recorded by a Varian XL-200 spectrometer with $CDCl_3$ as solvent using tetramethylsilane as the internal standard. UV spectra were measured by a Jasco Ubest-35 spectrometer. The number-average molecular weight $(\overline{M}_n)$ and weight-average molecular weight $(\overline{M}_w)$ were determined by means of gel permeation chromatography by using polystyrene calibration standards on a Tosoh HLD-803 apparatus.

RESULTS AND DISCUSSION

It is well known that chlorine atoms attached directly to the 1,3,5-triazine ring are very reactive and can be readily displaced by nucleophilic reagents [12, 19–21]. Therefore, we hoped that many types of functional monomers would be prepared by treatment of 2,4-dichloro-6-p-vinylphenyl-1,3,5-triazine (1) with nucleophiles such as amine, alkoxide, and mercaptide. Vinyl groups activated by electron-withdrawing triazine groups are often attacked by nucleophiles [22]. Therefore, in order to prevent the latter reaction, the conversion of 1 to 2,4-bis(diethylamino)-6-p-vinylphenyl-1,3,5-triazine (2) was carried out at low temperature by using diethylamine. Other monomers, 2,4-diethoxy-6-p-vinylphenyl-1,3,5-triazine (3), 2,4-bis(1,4,7-trioxaoctyl)-6-p-vinylphenyl-1,3,5-triazine (4), and 2,4-bis(ethylthio)-6-p-vinylphenyl-1,3,5-triazine (5), were similarly prepared by the reaction of the corresponding alkoxides and mercaptide in THF. The structures were confirmed by IR and NMR spectroscopies and elemental analysis.

	Nu
2	$N(C_2H_5)_2$
3	OC_2H_5
4	$O(CH_2CH_2O)_2CH_3$
5	SC_2H_5

Homopolymerization of these monomers 2–5 by AIBN in benzene at 60°C was carried out, and the results are summarized in Table 1. By the polymerization of 2, poly(2,4-bis(diethylamino)-6-p-vinylphenyl-1,3,5-triazine) (P-2) was obtained as the methanol-insoluble part in good yield (92%). In the IR spectrum of the polymer, two absorption bands based on terminal methylene at 905 and 990 cm^{-1} were absent. Furthermore, in the NMR spectrum, the signals of vinyl protons completely disappeared. These results show that this polymerization proceeds via ordinary radical mechanism. Other monomers (3–5) were also polymerized readily to afford the corresponding polymers as white solids in high yields. The number-average molecular weights ($\overline{M}_n$) are 31,000–52,000 and the polydispersities ($\overline{M}_w/\overline{M}_n$) of these monomers were 4.1–9.6. Here, polydispersity of P-5 is especially large and ($\overline{M}_n$) of P-5 is small in comparison with other polymers, which indicate that a chain transfer reaction occurred in the polymerization of 5. This fact could be understood by the fact that the α-hydrogen of divalent sulfur is well known to undergo abstraction by a free radical [23]. These polymers (P-2–5) are soluble in benzene, chloroform, tetrahydrofuran, and dimethylsulfoxide, but insoluble in n-hexane and methanol.

Next, in order to examine the reactivity of these monomers in radical copolymerization, copolymerization of 2–5 (M_1) with styrene (M_2) in benzene at various compositions of monomer feed was carried out at 60°C using AIBN as the initiator. The polymer yield was kept below 10% to evaluate the copolymerization parameters. The composition of the copolymers was determined by elementary analysis of carbon and nitrogen. Figures 1 and 2 show the monomer–copolymer composition curves.

Monomer reactivity ratios (r_1, r_2) in the above polymerizations were estimated by the Fineman–Ross method, and the resonance stabilization factor Q and electrical factor e values by Alfrey–Price were also calculated. They are all shown in Table 2. The Q values of these monomers are larger than that of styrene (1.0), and somewhat larger than 4-vinylbiphenyl (1.32) [24]. This result suggests that the benzene ring and the triazine ring exist in coplanarity, and that the π-orbitals of these aromatic rings are able to overlap. On the other hand, Ito et al. reported that a linear correlation of Q values with λ_{max} due to the π-π* transition is observed for many monomers [25]. So, Q values and λ_{max} for these monomers and their analogues as cited in Table 2 are related in Fig. 3. As can be seen from this figure, a linear correlation between Q values and λ_{max} of the π-π* transition was also observed

TABLE 1. Homopolymerization of Triazinylstyrene Derivatives Initiated by AIBN at 60°C[a]

Monomer	Yield, %	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	Sample
2	92	52,000	4.1	P-2
3	77	42,000	4.8	P-3
4	71	39,000	5.2	P-4
5	72	31,000	9.6	P-5

[a]Conditions: [Monomer] = 1.0 mol/L, [AIBN] = 0.01 mol/L, solvent = benzene, time = 20 hours.
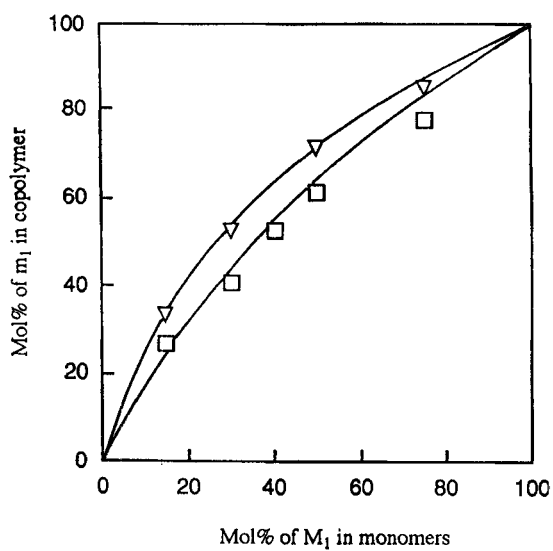
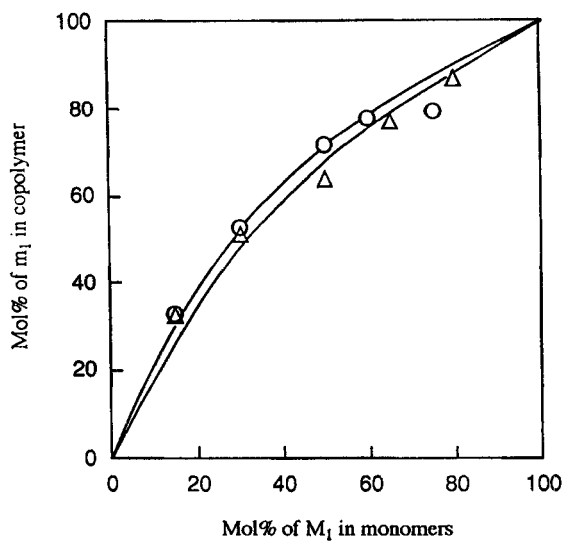FIG. 1. Monomer-copolymer composition curves of **2** (□) and **5** (∇) (M_1) with styrene (M_2).

FIG. 2. Monomer-copolymer composition curves of **3** (○) and **4** (△) (M_1) with styrene (M_2).

TABLE 2. Copolymerization Parameters of the Copolymerization of Triazinylstyrenes (M_1) and Styrene (M_2) in Benzene at 60°C, λ_{max}, and ^1H Chemical Shifts of Triazinylstyrenes

M_1	r_1	r_2	Q_1	e_1	λ_{max},[a] nm	Chemical shift,[b] ppm
1[c]	2.38	0.20	2.42	0.08	319	5.50
2	1.50	0.39	1.43	0.06	282	5.26
3	1.94	0.30	1.85	−0.06	294	5.41
4	1.51	0.29	1.67	0.11	294	5.38
5	1.82	0.26	1.94	0.07	301	5.40
Styrene			1.0	−0.8	254	5.18
4-Vinylbiphenyl[d]			1.32	−1.12	274[e]	5.24

[a]λ_{max} at π-π^* transition in ethanol.
[b]*trans* β-Proton in $CDCl_3$.
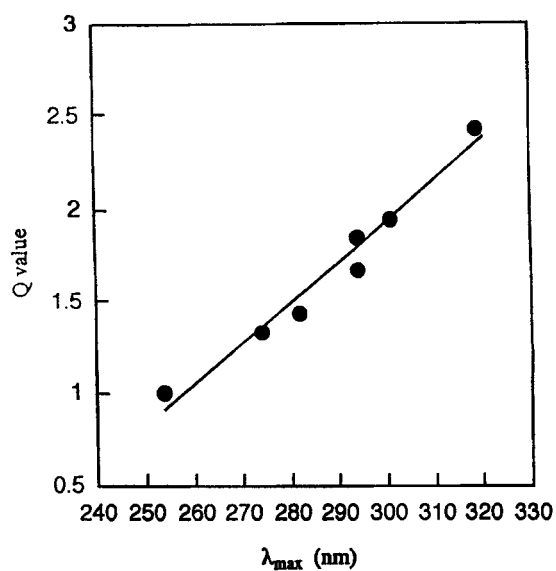[c]Ref. 12.
[d]Ref. 24.
[e]In hexane.

FIG. 3.   Plots of λ_{max} against Q.

for these monomers. Further, e values of these monomers are between -0.06 and 0.11. These values are larger than that of styrene (-0.8), and the difference of e values among these monomers is very small. These results indicate that triazine ring itself has a strong electron-withdrawing character. This explanation is supported by the fact that chemical shifts of the *trans-β*-proton of these monomers are in lower fields than that of styrene (Table 2).

CONCLUSION

Several triazinylstyrene derivatives as reactive monomers carrying two functional groups were readily prepared by the reaction of 2,4-dichloro-6-p-vinylphenyl-1,3,5-triazine with nucleophilic reagents under mild conditions. These monomers polymerized with AIBN to afford the corresponding polymers in high yields. From copolymerization with styrene, copolymerization parameters (r_1, r_2, Q, e) were estimated. The larger Q values than that of styrene indicate the coplanarity of the benzene ring and the triazine ring. The effect of substitutents attached directly to the triazine ring on the e value was very small because the triazine ring itself has a strong electron-withdrawing character.

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