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Preparation and Free-Radical Polymerization of 2,4-Dichloro-6-(*p*-Vinylphenyl)-1,3,5-triazine as a Reactive Monomer Containing Two Replaceable Groups

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PREPARATION AND FREE-RADICAL POLYMERIZATION OF 2,4-DICHLORO-6-(*p*-VINYLPHENYL)-1,3,5-TRIAZINE AS A REACTIVE MONOMER CONTAINING TWO REPLACEABLE GROUPS

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ABSTRACT

A new monomer containing two replaceable groups, 2,4-dichloro-6-(*p*-vinylphenyl)-1,3,5-triazine (DCVT) was prepared by the reaction of *p*-vinylphenylmagnesium chloride with cyanuric chloride. This monomer was polymerized readily in benzene by AIBN at 60°C. From the copolymerization with styrene, Q and e values of DCVT were obtained as $Q = 2.42$ and $e = 0.08$. An insoluble terpolymer prepared from DCVT, styrene, and divinylbenzene was treated with several nucleophilic reagents, including sodium methoxide, sodium methylmercaptide, dimethylamine, and triethylphosphite, to afford the corresponding polymers in high conversions.

INTRODUCTION

Polymer-supported catalysts and reagents recently developed have become useful in organic synthesis [1, 2]. The main advantages of these polymers are the easy separation of product and the recovery of the polymers. Polymer catalysts occasionally display higher activity than their monomeric analogs [3–14]. The difference is mainly due to a cooperative effect of neighboring groups along the polymer backbone and the formation of an attractive microenvironment around the active sites.

This cooperative effect generally increases with an increasing density of active site, while the increasing density reduces the formation of a hydrophobic microenvironment. Therefore, one approach to obtaining a polymer catalyst with high activity is to design it with monomers containing several functional groups. These functional monomers are generally prepared by the substitution reaction of reactive monomers having several replaceable groups. Desirable polymer catalysts would be obtained by copolymerization of such functional monomers with hydrophobic vinyl monomers. However, there are few reports on vinyl monomers containing several replaceable groups [15–18].

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 [19]. Therefore, we hoped that polymers containing dichlorotriazine would work as reactive polymers containing two functional groups in a monomer unit. Manecke and Rewicki reported the synthesis of polymers containing such a moiety [15]. However, the polymers prepared by them contained other functional groups such as ether and amide except for chlorine. These groups are sometimes not desirable as polymer supports. We recently prepared poly(2,4-dichloro-6-vinyltriazine-*co*-styrene)s by using poly(2,4-diamino-6-vinyltriazine-*co*-styrene)s as the starting polymers [20]. However, this method required a long time and the conversion was not quantitative.

In this article we describe the preparation of styrene attached directly to a dichlorotriazine moiety, polymerization of this monomer, copolymerization with styrene, and the reaction of these copolymers with various nucleophiles.

EXPERIMENTAL

Materials

Styrene, *p*-chlorostyrene, commercial divinylbenzene (DVB) containing 45% ethylstyrene and diethylbenzene, 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. 2,4-Dimethoxy-6-phenyl-1,3,5-triazine [21], 2,4-bis(dimethylamino)-6-phenyl-1,3,5-triazine [22], 2,4-bis(diethoxyphosphinyl)-6-phenyl-1,3,5-triazine [23], and 2,4-dimethylthio-6-phenyl-1,3,5-triazine [24] were prepared as model compounds according to literature methods.

Preparation of 2,4-Dichloro-6-(*p*-vinylphenyl)-1,3,5-triazine

A solution of *p*-vinylphenylmagnesium chloride, prepared from magnesium (14.59 g, 0.60 mol) and *p*-chlorostyrene (42.22 g, 0.30 mol) in tetrahydrofuran (THF) (160 mL) was added slowly to a stirred solution of cyanuric chloride (83.0 g, 0.45 mol) in THF (300 mL). After stirring at room temperature for 10 hours, 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 33.8 g (45%), mp 116°C.

NMR (in $CDCl_3$): δ = 5.46 (1H, d), 5.95 (1H, d), 6.78 (1H, dd), 7.50 (2H, d) and 8.41 ppm (2H, d). IR: $\nu_{C=CH_2}$ = 930 and 980 cm^{-1}. UV (in ethanol): λ_{max} = 319 nm (ϵ = 29,000).

Analysis. Calculated for $C_{11}H_7Cl_2N_3$: C, 52.48; H, 2.80; Cl, 28.13; N, 16.67%. Found: C, 52.71; H, 2.67; Cl, 28.25; N, 16.46%.

Polymerization Procedure

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 [25]. The tube was opened after polymerization, and its contents were poured into a large amount of ether to precipitate the polymer. The resulting polymer was purified by reprecipitation from chloroform with ether. The copolymer composition was evaluated from the chlorine content.

Preparation of Insoluble Polymer Support P1

A mixture of DCVT (15.00 g, 59.5 mmol), styrene (33.02 g, 317 mmol), commercial DVB (4.71 g, 19.9 mmol), AIBN (0.41 g, 2.5 mmol), and benzene (150 mL) was heated at 60°C for 24 hours under nitrogen. The resulting gel was treated with Soxhlet extraction using benzene as solvent and followed by drying. The yield was 47.81 g. The chlorine content of this polymer, P1, was 9.82%. From this result, the content of DCVT in the copolymer was determined to be 18.1%. The DVB content was assumed to be identical to the monomer feed.

Reaction of P1 with Dimethylamine

A mixture of P1 (5.0 g, 6.61 mmol based on the dichlorotriazine unit), 50% aqueous dimethylamine (3.71 g, 41.14 mmol), and THF (100 mL) was stirred at reflux temperature. After 50 hours the reaction mixture was poured into water. The polymer, P2a, was filtered, washed with THF and benzene, and then treated with Soxhlet extraction by using benzene for 24 hours. The yield was 4.20 g.

Analysis: Cl, 0.82%.

Reaction of P1 with Sodium Methoxide

To a mixture of sodium hydride (~60%, oil suspension, 0.78 g, 19.50 mmol) and THF (75 mL) was added methanol (0.58 g, 18.10 mmol), and the system was refluxed for 1 hour. After cooling to room temperature, P1 (2.75 g, 2.43 mmol based on the dichlorotriazine unit) was added and further refluxed for 40 hours. Then the reaction mixture was poured into water and filtered. The polymer was swelled with THF and washed with water. This work-up was repeated several times. After treatment with Soxhlet extraction with benzene for 24 hours, the polymer was dried. The yield of P2b was 2.67 g.

Analysis: Cl, 0.54%.

Reaction of P1 with Triethylphosphite

A mixture of P1 (2.50 g, 3.43 mmol based on the dichlorotriazine unit), triethylphosphite (5.70 g, 34.30 mmol), and THF (50 mL) was refluxed for 72 hours with stirring. Then the polymer was filtered and washed thoroughly with benzene. After treatment with Soxhlet extraction with benzene for 24 hours, the polymer was dried. The yield of P2c was 2.84 g.

Analysis: Cl, 0.14%.

Reaction of P1 with Sodium Mercaptide

A mixture of P1 (2.50 g, 3.43 mmol based on the dichlorotriazine unit), 15% aqueous sodium methylmercaptide (10.00 g, 21.40 mmol), and THF (70 mL) was stirred at 60°C for 50 hours. The polymer was filtered and washed thoroughly with water and THF successively. After treatment with Soxhlet extraction with benzene for 24 hours, the polymer was dried. The yield of P2d was 1.79 g.

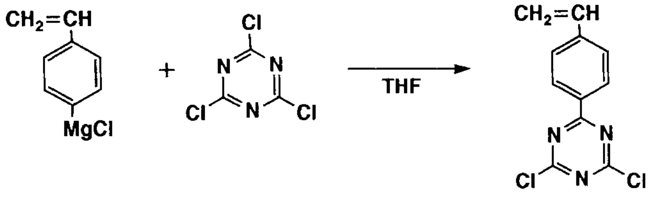
Analysis: Cl, 0.96%.

Measurements

IR spectra were measured by a Hitachi R-285 spectrometer. NMR spectra were recorded by a Hitachi R-20 B spectrometer with $CDCl_3$ as solvent using tetramethylsilane as the internal standard. UV spectra were measured by a JASCO Ubest-35 spectrometer. Gel permeation chromatography (GPC) was carried out on a TOSOH HLC-803D with G2000, G3000, and GMH TSK gel-columns and a differential refractometric detector in tetrahydrofuran.

RESULTS AND DISCUSSION

Synthesis of the vinyl monomer was carried out by the use of *p*-vinylphenylmagnesium chloride.



(1)

DCVT

The DCVT obtained was a white solid, soluble in ordinary organic solvents. The IR spectrum exhibited a characteristic terminal double bond at 930 and 990 cm^{-1}. The NMR spectrum consisted of peaks at 5.46–6.78 ppm for vinyl protons and at 7.50–8.41 ppm for aromatic protons. These signals shifted remarkably downfield compared with those of styrene. This fact indicates that the dichlorotriazine moiety has a strong electron-withdrawing character. The UV spectrum showed an absorption band of $\pi \rightarrow \pi^*$ transition at 319 nm in ethanol, whereas the absorption spectrum of

TABLE 1. Homopolymerization of DCVT and Copolymerization of Styrene (M_1) with DCVT (M_2) Initiated by AIBN at 60°C[a]

Feed				Polymer		
M_1, mmol	M_2, mmol	Time, min	Conversion, %	N, %	m_2, mol %	$M_n \times 10^{-4}$[b]
8.5	1.5	300	13.5	10.17	39.5	2.7
7.2	3.1	260	10.9	12.59	56.5	2.3
5.0	5.0	210	10.1	14.57	74.2	1.8
4.0	6.0	120	10.8	15.27	81.4	2.2
2.5	7.5	90	7.3	15.85	89.5	—[c]
0	10	60	8.9		100	—[c]

[a] AIBN = 0.1 mmol, benzene = 10 mL.

[b] Determined by GPC.

[c] Not soluble in THF.

styrene was at 248 nm. This observation can be explained by the assumption that the benzene ring and the triazine ring exist in coplanarity and overlap the π-orbitals of these aromatic rings.

Polymerization of DCVT

DCVT was polymerized smoothly by AIBN to give a white powder which was not soluble in benzene or THF. In order to obtain the polymerization parameters, copolymerization with styrene was investigated. The results are shown in Table 1. Figure 1 shows the monomer–copolymer composition curve.

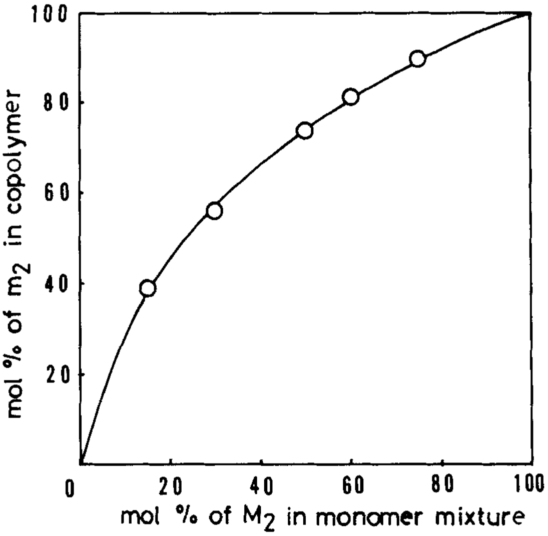
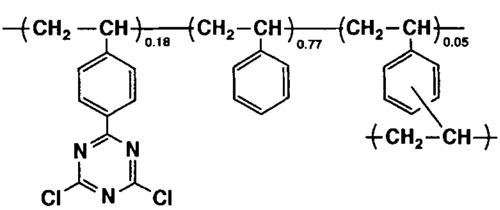


FIG. 1. Monomer–copolymer composition curve of styrene (M_1) and DCVT (M_2).

The monomer reactivity ratios were computed according to the Fineman-Ross method as $r_{DCVT} = 2.38$, $r_{St} = 0.20$. From these values for this copolymerization, the resonance stabilization factor Q and the electrical factor e of DCVT were calculated as $Q = 2.42$ and $e = 0.08$. This large Q value is reflected by the coplanarity of the benzene ring and the triazine ring as indicated by the UV spectrum mentioned above. Further, the positive e value is reasonable because of the strong electron-withdrawing character of the dichlorotriazine ring.

Preparation of Polymer Support P1

Terpolymerization of DCVT, styrene, and divinylbenzene in benzene by AIBN afforded the gel-type of polymer P1:

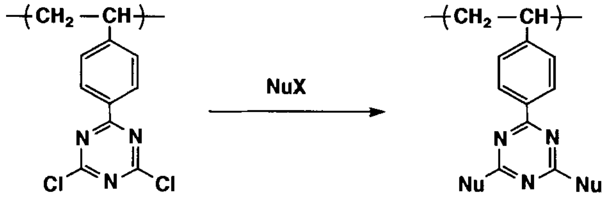


P1

The polymer was crushed and separated to 60–100 mesh before use.

Reaction of P1 with Various Nucleophiles

The availability of P1 as a reactive polymer was examined for several nucleophilic aromatic substitution reactions as shown in Eq. (2). The results are summarized in Table 2.



P1 P2 (2)

	Nu
P2a	$N(CH_3)_2$
P2b	OCH_3
P2c	$P(O)(OC_2H_5)_2$
P2d	SCH_3

When P1 and aqueous dimethylamine were heated in THF at 60°C for 50 hours, the corresponding polymer (P2a) was obtained in 95% yield. The reaction with methoxide also took place quantitatively. Further, the reaction of P1 with sodium mercaptide gave the corresponding polymer containing the mercaptotriazine moiety (P2d) in high yield. In addition, by using triethylphosphite in the Arbuzov

TABLE 2. Reaction of Crosslinked Polymer P1 with Several Nucleophilic Reagents[a]

Reagent	[Cl]/[reagent]	Time, h	Conversion, %	Polymer
$(CH_3)_2NH$ (50% in H_2O)	6	50	91	P2a
CH_3OH, NaH	6	40	92	P2b
$(C_2H_5O)_3P$	10	72	98	P2c
CH_3SNa (15% in H_2O)	6	50	90	P2d

[a] Reaction conditions: solvent = THF, temperature = 60°C.

reaction a polymer containing phosphinyl groups (P2c) was obtained. The structures were confirmed by comparing the IR spectra with those of the corresponding monomeric compounds and by elemental analysis. Thus polymers having the dichlorotriazine moiety were found to work as polymer supports containing two replaceable groups in their monomer unit.

CONCLUSION

A new substituted styrene, 2,4-dichloro-6-(*p*-vinylphenyl)-1,3,5-triazine, was prepared by the use of *p*-vinylphenylmagnesium chloride and cyanuric chloride. This monomer was polymerized readily in benzene by AIBN. From the copolymerization with styrene, the copolymerization parameters were obtained. The large *Q* value (2.42) was understood after consideration of the coplanarity of the benzene ring and the triazine ring. An insoluble polymer prepared from the terpolymerization of this monomer, styrene, and divinylbenzene served as a polymer support containing two replaceable groups in a monomer unit.

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