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Synthesis and polymerization of 4-vinyl [2.2]paracyclophane

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SUMMARY

4-Vinyl [2.2]paracyclophane (1) was successfully prepared as white crystals in 45 % yield via three step reactions. Monomer 1 was homopolymerizable with 2,2'-azobis(isobutyronitrile) (AIBN), boron trifluoride etherate, and butyllithium. Monomer 1 was copolymerizable with methyl acrylate and p-chlorostyrene in the presence of AIBN in benzene at 60 ℃. It was found that monomer 1 was less conjugative and more electron-donating than styrene.

INTRODUCTION

Since [2.2]paracyclophane was discovered and characterized by Brown and Farthing (1), many kinds of cyclophane compounds have been prepared and their properties and reactivity have been studied (2). As [2.2]paracyclophane produces very reactive biradical or quinodimethane intermediate on heating, some polymers containing [2.2]-paracyclophane unit in the backbone had been prepared in order to develop new process for crosslinking resins without liberating gaseous side products (3-6). However, preparation of polymers by the polymerization of vinyl type monomers carrying [2.2]paracyclophane unit has not been reported yet.

In this work, 4-vinyl [2.2]paracyclophane (1) was first prepared as a new vinyl type monomer with [2.2]paracyclophane unit and its polymerization behavior was studied and compared with that of styrene (St).

EXPERIMENTAL

4-Acetyl [2.2]paracyclophane (3)

[2.2]Paracyclophane (2) (5.02 g, 24 mmol) was added to

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the suspension of 6.06 g (45.4 mmol) of aluminum chloride and 3.80 g (48.4 mmol) of acetyl chloride in 45 mL of 1,1,2,2-tetrachloroethane at -38 ℃ , and then the mixture was stirred for 3 h under nitrogen. Into the reaction mixture was added 20 mL of 1N hydrochloric acid and organic layer was separated. Water layer was extracted with chloroform. The organic layer and extracts were combined, washed with water, 3 % sodium bicarbonate aqueous solution, and dried over anhydrous magnesium sulfate. It was placed under reduced pressure to remove volatile materials to give yellow solid, which was recrystallized from a mixture of ethanol and water to afford 5.36 g (yield 88.5 %) of compound 3 as white plate: mp 109.0 ~ 109.5 ℃ (109.7 ~ 110.4 ℃ (7)); IR(KBr): $\nu_{C=O}$ 1648, σ_{CH} 943 cm^{-1}; ^{1}H NMR($CDCl_3$): δ 6.93 ~ 6.36 (m, 7H), 3.20 ~ 2.78 (m, 8H), 2.47 (s, 3H); ^{13}C NMR($CDCl_3$): 200.2 (C=O), 141.5 ~ 131.1 (aromatic), 36.0, 34.9 ($-CH_2-$), 28.7 ($-CH_3$). Anal. Calcd for $C_{18}H_{18}O$: C, 89.98; H, 3.36; O, 6.66. Found: C, 89.76; H, 3.38.

4-(1'-Hydroxyethyl) [2.2]paracyclophane (4)

Sodium borohydride (3.13 g, 82.7 mmol) was added to 5.73 g (16.4 mmol) of compound 3 in 100 mL of methanol and then the mixture was stirred at room temperature for 3 h. The reaction mixture was placed under reduced pressure to remove methanol to give white solid, which was dissolved in 50 mL of dichloromethane. The resulting solution was washed with dilute hydrochloric acid, water and dried over anhydrous magnesium sulfate. It was placed under reduced pressure to remove solvent to afford white solid, which was recrystallized from a mixture of ethanol and water to afford 4.83 g (yield 83.6 %) of compound 4 as white needles: mp 79.0 ~ 82.0 ℃; IR(KBr): ν_{OH} 3340, ν_{C-O} 1052 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.63 ~ 6.34 (m, 7H), 4.94 ~ 4.86 (m, 1H), 3.38 ~ 2.77 (m, 8H), 1.72 (s, 1H), 1.34 ~ 1.22 (m, 3H); ^{13}C NMR($CDCl_3$): 144.7 ~ 128.1 (aromatic), 67.8, 67.4 ($-CH-$), 35.3, 35.2, 35.1, 34.7, 34.3, 33.2, 33.1, 30.8 ($-CH_2-$), 25.7 ($-CH_3$). Anal. Calcd for $C_{18}H_{20}O$: C, 85.66; H, 8.00; O, 6.34. Found: C, 85.71; H, 8.01.

4-Vinyl [2.2]paracyclophane (1)

Cupper(II) sulfate pentahydrate (61.5 mg, 0.25 mmol) and 34.6 mg (0.31 mmol) of hydroquinone were added to 4.83 g(19.1 mmol) of compound 4 in 200 mL of toluene and then the mixture was refluxed for 3 h. The reaction mixture was filterd on celite and placed under reduced pressure to remove toluene to give pale yellow solid, which was dissolved in 50 mL of chloroform. The resulting solution was washed with water, 2 % sodium bicarbonate aqueous solution, and dried over anhydrous magnesium sulfate. It was placed under reduced pressure to remove chloroform to afford yellow solid, which was dissolved in a small amount of hexane. The resulting solution was passed through a silica gel column by using hexane as an eluent. The first elution band part was collected and placed under reduced pressure to remove hexane to obtain white solid, which was recrystallized from a mixture of ethanol and water to afford 2.72 g (yield 60.6 %) of compound 1 as white needles: mp 79.0 ~ 80.0 ℃; IR(KBr): ν_{CH} 2888, $\delta_{CH=CH_2}$ 978, 899 cm^{-1}; ^{1}H NMR(CDCl$_3$): δ 6.85 ~ 6.70 (m, 1H), 6.55 ~ 6.38 (m, 7H), 5.57 ~ 5.50 (m, 1H), 5.30 ~ 5.26 (m, 1H), 3.52 ~ 2.74 (m, 8H); ^{13}C NMR(CDCl$_3$): 139.7 ~ 130.0 (aromatic), 132.9, 114.1 (-CH=CH$_2$), 35.3, 35.1, 34.5, 33.5 (-CH$_2$-). Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.12; H, 7.88.

Other Materials

2,2'-Azobis(isobutyronitrile)(AIBN) was recrystallized from methanol. Boron trifluoride etherate was distilled under reduced pressure in an atomsphere of nitrogen. Commercial butyllithium (Aldrich Co.) was used without further purification. Methyl acrylate (MA) and p-chlorostyrene (ClSt) were distilled twice from calcium hydride before use. Benzene and toluene were purified by distillation from metal sodium and dichloromethane from calcium hydride, respectively.

Polymerization Procedure

In the case of ionic polymerization with boron trifluoride etherate and butyllithium, the polymerization was carried out under nitrogen and dry condition by using the apparatus reported previously (8). After the time of polymerization, the reaction mixture was poured into an excess of methanol to deposit a polymeric product, which was dissolved in a small amount of tetrahydrofuran and the resulting solution was poured again into an excess of methanol for purification. The polymeric product obtained was dried under reduced pressure until a constant weight.

In the case of radical homopolymerization and copolymerization with AIBN, given amounts of monomer 1, MA or ClSt as a comonomer and benzene as a solvent if necessary, and AIBN as an initiator were placed in an ampule, which was degassed by the freeze-thaw method (repeated three times) and sealed. The ampule was set in a bath thermostated at 60 or 85 ℃ for the time of polymerization. The rest of the procedure was carried out similarly to the above-mentioned ionic polymerization.

Characterization

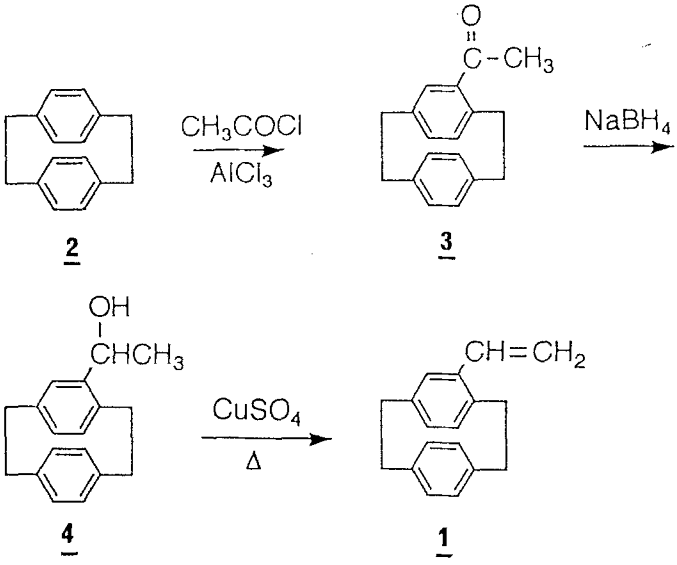
Copolymer composition was established by elemental analysis. Number-average molecular weights, $\overline{M}n$, of homopolymers and copolymers were determined by gel permeation chromatography (GPC) using standard polystyrenes as reference and tetrahydrofuran as an eluent without correction. ^{1}H- and ^{13}C-NMR measurements were carried out in chloroform-d with tetramethylsilane as an internal standard. Glass transition temperature (Tg) for homopolymer was determined by differential scanning calorimetry (DSC) at an elevating rate of 10 ℃/min under nitrogen (30 mL/min).

RESULTS AND DISCUSSION

Synthesis of Monomer 1

Monomer 1 was successfully prepared according to Scheme I.

Scheme I



[2.2]paracyclophane (2) was subjected to Friedel-Crafts reaction with acetyl chloride at -38 ℃ to give 4-acetyl [2.2]paracyclophane (3) in good yield. The carbonyl group in compound 3 was easily reduced to hydroxy one with sodium borohydride to give 4-(1'-hydroxyethyl) [2.2]paracyclophane (4) in good yield. The 1-(hydroxy)ethyl group in compound 4 was converted easily to vinyl one by dehydration reaction in the presence of copper(II) sulfate pentahydrate to obtain 4-vinyl [2.2]paracyclophane (1) as white needles. Its IR, ^{1}H- and ^{13}C-NMR spectra, and elemental analysis strongly suggested the chemical structure of the monomer 1.

Table 1. Homoloymerizations of Monomer 1 with Various Initiators

Run no.	Monomer 1, mg	Initiator I	$\frac{[M]}{[I]}$	Solvent mL	Temp. ℃	Time h	Yield mg	Convn. %	$\frac{\overline{M}_n}{10^3}$
1	230	AIBN	35	PhH,1.0	60	5	0		
2	230	AIBN	52	PhH,0.5	60	5	trace		
3	235	AIBN	75	PhH,0.2	60	5	7	3	2.6
4	50	AIBN	14	Bulk	85	5	17	34	5.4
5	115	BF_3OEt_2	18	CH_2Cl_2,3.0	0	12	0		
6	117	BF_3OEt_2	10	CH_2Cl_2,0.5	0	20	84.2	72	4.0
7	31	BuLi	8	PhMe,1.0	0	12	0		
8	375	BuLi	10	PhMe,1.7	0	18.5	328	87.5	2.0

Homopolymerization

Homopolymerization of monomer 1 was attempted with various initiators such as AIBN, boron trifluoride etherate, and butyllithium as summarized in Table 1.

When the monomer concentration was as low as 0.82 mol/L (run no. 1), the polymerization of monomer 1 with AIBN at 60 ℃ failed to obtain polymeric product. Unreacted monomer 1 was recovered in a quantitative amount. On the other hand, when the monomer concentration was 1.43 mol/L (run no. 2) and 2.58 mol/L (run no. 3), monomer 1 was able to polymerize at 60 ℃ to give trace amount of the polymer and 7 mg (convn. 3 %) of the polymer with $\overline{M}n$ of 2600, degree of polymerization ($\overline{DP}$) of 11, respectively. Bulk polymerization of monomer 1 with AIBN, corresponding to the monomer concentration of 5.33 mol/L (run no. 4), was carried out at 85 ℃ to give 17 mg (convn. 34 %) of the polymer with $\overline{M}n$ of 5400, $\overline{DP}$ of 23. While, bulk polymerization of St with AIBN under the same condition gave polystyrene with $\overline{M}n$ of 13000, $\overline{DP}$ of 125, in quantitative yield, indicating that monomer 1 is less reactive than St. The polymerization of monomer 1 by boron trifluoride etherate with a monomer concentration of 0.16 mol/L in dichloromethane at 0 ℃ failed to obtain polymeric product. While, when the monomer concentration was as high as 0.84 mol/L, polymerization of monomer 1 occurred to give 84.2 mg (convn. 72 %) of the polymer with $\overline{M}n$ of 4000, $\overline{DP}$ of 17. The polymerization of monomer 1 by butyllithium with a monomer concentration of 0.13 mol/L in toluene at 0 ℃ failed to obtain polymeric product. While, when the monomer concentration was as high as 0.74 mol/L, polymerization of monomer 1 took place to afford 328 mg (convn. 87.5 %) of the polymer with $\overline{M}n$ of 2000, $\overline{DP}$ of 8. Polymerization of monomer 1 with high monomer concentration was found to take place slowly although molecular weight and yield of the polymers obtained were considerably low. As the cyclophane unit in monomer 1 is bulky, it is likely to have lower ceiling temperature. ^{1}H NMR and IR spectra of all polymers obtained suggested the polymerization at the vinyl group of monomer 1. It was found that monomer 1 is homopolymerizable with radical, cationic, and anionic initiators as well as St.

Polymer of 1 was soluble in toluene, benzene, chloroform, dichloromethane, and tetrahydrofuran, and insoluble in methanol, hexane, and diethyl ether. The polymers (run nos. 4 and 6) could be cast into transparent but brittle films, probably due to their low molecular weights. The Tg of the polymer (run no. 4) was determined by DSC to be 130 ℃, which is higher than that of polystyrene (Tg= 100.5 ℃) (9).

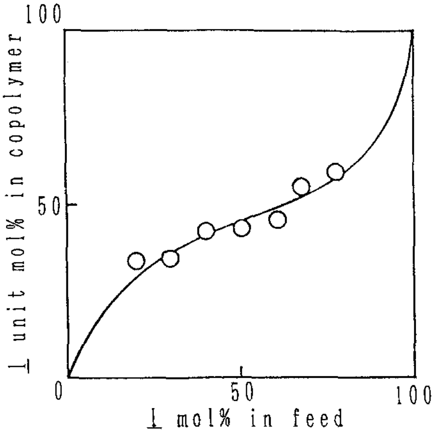
Copolymerization

The copolymerizations of monomer 1 with MA and with ClSt were carried out in benzene at 60 ℃ with a given monomer concentration of monomer 1 of 2 mol/L. These results are shown in Table 2 and their copolymerization composition diagrams are shown in Figures 1 and 2. The results of the

Table 2. Copolymerizations of Monomer 1 with Methyl Acrylate (MA) and with p-Chlorostyrene (ClSt) in Benzene[a] at 60 ℃

Run	Feed, mg		1	AIBN	Time	Convn.		Anal.		Compn.	M_n
no.	1	M_2	mol%	mg	h	%	%H	%C	%Cl	1 mol%	10^3
					M_2 : MA						
1	234.8	346.1	20.0	4.8	5.5	4.5	7.50	76.95		33.7	15
2	233.3	202.2	29.8	3.6	5.5	3.5	7.65	77.18		34.2	10
3	234.5	130.1	39.9	3.2	5	2.5	7.75	80.12		42.4	7
4	234.5	86.0	50.1	3.1	5	3.1	7.62	80.14		42.5	5
5	232.9	56.4	60.3	3.0	17	5.7	7.74	81.19		45.7	4
6	235.9	41.4	67.7	3.3	17	3.9	7.72	83.89		55.2	4
7	234.4	24.6	77.8	3.3	17	2.8	7.80	85.06		59.9	3
					M_2 : ClSt						
8	234.8	552.7	20.1	4.0	3	7.3	5.83	73.93	20.24	13.5	45
9	233.1	325.6	29.8	3.4	3	5.1	6.05	75.91	18.04	19.8	30
10	233.9	205.2	40.3	2.8	3	2.6	6.25	77.56	16.19	25.5	19
11	233.2	141.5	48.6	2.7	3	2.0	6.54	79.46	14.00	32.9	15
12	234.2	91.2	60.3	2.7	17	8.0	6.90	84.43	8.67	53.6	10
13	233.5	56.6	70.9	3.2	4	1.8	6.94	84.94	8.12	56.0	6
14	231.5	33.0	80.6	3.7	17	4.5	7.40	87.84	4.76	72.1	4
15	234.5	15.0	90.2	2.7	17	2.2	7.56	89.80	2.64	83.7	3

a) [1] = 2 mol/L.



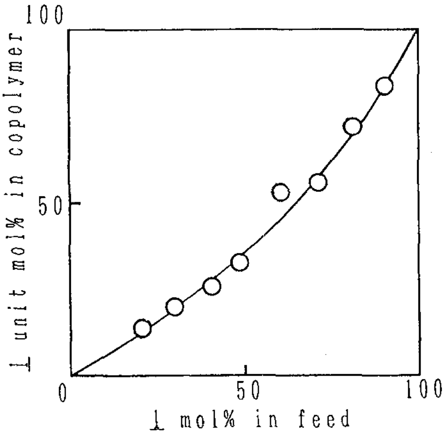


Figure 1 Copolymerization composition diagram for the 1-MA system

Figure 2 Copolymerization composition diagram for the 1-ClSt system

copolymerizations were analyzed with the intersection and Kelen-Tüdös methods to obtain monomer reactivity ratios: r_1(1) = 0.15 ± 0.10 and r_2(MA) = 0.38 ± 0.10 at 60 ℃ for the 1-MA system and r_1(1) = 0.52 ± 0.20 and r_2(ClSt) = 1.80 ± 0.40 at 60 ℃ for the 1-ClSt system, respectively. The copolymerizations of styrene (St) with MA and with ClSt at 60 ℃ were reported to give monomer reactivity ratios: r_1(St) = 0.75 ± 0.03 and r_2(MA) = 0.18 ± 0.02 for the St-MA system (10) and r_1(St) = 0.74 ± 0.025 and r_2(ClSt) = 1.025 ± 0.05 for the St-ClSt system (10), respectively. Comparison with the reciprocal, $1/r_2$, of the monomer reactivity ratio allowed a relative reactivity of monomer 1 and St toward the polymer radical with MA terminal unit being MA (1) < 1 (2.63) < St (5.56) and toward the polymer radical with ClSt terminal unit being 1 (0.56) < St (0.98) < ClSt (1), respectively, indicating that monomer 1 is less reactive than St. Alfrey-Price's Q and e values of monomer 1 were calculated on the basis of the monomer reactivity ratios to be Q = 0.4 and e = - 1.1 for the 1-MA system and to be Q = 0.87 and e = -0.90 for the 1-ClSt system, respectively. Monomer 1 is less conjugative and more electron-donating than St, probably being attributable that resonance between vinyl group and aromatic ring in [2.2]paracyclophane unit is forbidden by distortion of its aromatic ring and that electron density of vinyl group is increased directly (through bond) and/or indirectly (through space) by another aromatic ring.

CONCLUSION

4-Vinyl [2.2]paracyclophane (1) was successfully prepared in 45 % yield via three step reactions. Monomer 1 was homopolymerizable with radical, cationic, and anionic initiators. Monomer 1 was copolymerizable with MA and with ClSt in the presence of AIBN in benzene at 60 ℃. It was found that monomer 1 was less conjugative and more electron-donating than St.

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