Preparation of 1,3,5-Trivinyl-2,4,6-trichlorobenzene and Its Copolymerization with Styrene

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INTRODUCTION

The present interest in cross-linking agents for vinyl monomers stems from three sources: (a) the widespread demand for polymers with high heat distortion temperatures, (b) the use of highly cross-linked polymers in the preparation of ion-exchange resins,¹ and (c) the new interest in polymer carbon.² In prior publications from this laboratory we have reported the preparation of 1,4-divinyl-2,3,5,6-tetrachlorobenzene and its copolymerization with styrene³ and the preparation of 1,3-divinyl-2,4,5,6-tetrachlorobenzene.⁴ It is our present purpose to describe the preparation and properties of a monomer of higher functionality, 1,3,5-trivinyl-2,4,6-trichlorobenzene, and to report studies which measure its effectiveness as a crosslinking agent for styrene and compare its copolymerization with that of the two cross-linking agents previously reported from this laboratory.^{3,4}

These chlorinated di- and trivinylbenzenes have the appreciable advantage of being readily obtainable as single pure isomers. They are crystalline solids at room temperature and can be rigorously purified by crystallization. Since they are solids, they can be stored without inhibitors and, more important, added to polymerization systems in precisely controlled amounts. It is this element of facile control which is their chief advantage over the commercially available divinylbenzenes, and, as will be shown, the rates of copolymerization as well as the physical properties permit simple control of polymerization systems.

PREPARATION OF 1,3,5-TRIVINYL-2,4,6-TRICHLOROBENZENE

1,3,5-Trivinyl-2,4,6-trichlorobenzene was prepared by the sequence of reactions shown below:





1,3,5-Triethylbenzene, I, was prepared by alkylation of benzene with ethyl bromide and aluminum chloride following the procedure of Norris and Rubinstein⁵ or isolated from commercial mixed triethylbenzenes (Alkazene 3 from The Dow Chemical Company) according to Smith and Guss.⁶ Chlorination of I in the presence of iron powder gave 55% of 1,3,5-triethyl-2,4,6-trichlorobenzene, II. Photocatalyzed bromination of II in carbon tetrachloride resulted in a quantative yield of 1,3,5-tris(α bromoethyl)-2,4,6-trichlorobenzene, III. III is obtained as a mixture of optical isomers, but since all points of asymmetry are destroyed in the dehydrohalogenation reaction, the mixture may be used without separation of the isomers. The dehydrohalogenation of III to give 1,3,5-trivinyl-2,4,6-trichlorobenzene, IV, was effected with alcoholic potassium hydroxide. The details of the preparations follow.

1,3,5-Triethyl-2,4,6-trichlorobenzene, II

1,3,5-Triethylbenzene (90 g.; 0.55 mole) and iron powder (0.55 g.) were placed in a 250 cc. 3-neck flask, fitted with a chlorine bubbler, a reflux condenser, and thermometer. Chlorine was added until the gain in weight was 60 g. During most of the addition the reaction temperature was maintained below 40° but was allowed to rise to 60° near the finish. Air was bubbled through the reaction m^{*}xture to remove hydrogen chloride and dissolved chlorine. The crude product was dissolved in benzene, and the solution was filtered free of iron powder, washed two times with 20% sodium hydroxide and dried over anhydrous magnesium sulfate. Distillation at 13 mm. gave a main fraction of 124 g.; b.p. 156–160°. Crystallization from methanol-ether gave II; m.p. 62–64.5°; yield 81 g. (54.7%). A sample crystallized three additional times for analysis had m.p. 65–66°.

ANAL. Calcd. for $C_{12}H_{15}Cl_3$: C, 54.28; H, 5.70. Found: C, 54.02, 53.81; H, 5. 88, 6.01.

1,3,5-Tris(α-bromoethyl)-2,4,6-trichlorobenzene, III

Bromine (144 g.; 0.9 mole) was added dropwise over an eight hour period to II (80 g.; 0.3 mole) in carbon tetrachloride (600 cc.) heated to reflux and illuminated with a 500 watt unfrosted bulb. The solution was washed with water and 10% sodium hydroxide and dried over magnesium sulfate. Removal of the solvent gave 150 g. of III; m.p. $125-140^{\circ}$, with prior softening at 100°. This product was used, without further purification, in the dehydrohalogenation reaction. A sample crystallized for analysis three times from ligroin had m.p. $155-156^{\circ}$. ANAL. Calcd. for $C_{12}H_{12}Cl_3Br_3$: C, 28.68; H, 2.41. Found: C, 28.57, 28.40; H, 2.62, 2.51.

1,3,5-Trivinyl-2,4,6-trichlorobenzene, IV

A solution of III (40 g.; 0.08 mole) and potassium hydroxide (26.8 g.; 0.48 mole) in absolute ethanol (500 cc.) was refluxed for 30 minutes with vigorous stirring. The reaction mixture was poured into three liters of water. The product was filtered and washed with a little cold methanol; yield 14 g. (67.5%); m.p. 57-60°. Recrystallization from methanol-ether (1:1) gave 9 g. (43.4%); m.p. 63-64°. A sample crystallized two additional times for analysis had m.p. 64.5-65°.

Anal. Calcd. for $C_{12}H_9Cl_3$: C, 55.57; H, 3.49. Found: C, 55.53, 55.24; H, 3.70, 3.87.

ABSORPTION SPECTRA

The infrared and ultraviolet absorption spectra of 1,3-divinyl-2,4,5,6-tetrachlorobenzene (V), 1,4-divinyl-2,3,5,6-tetrachlorobenzene (VI), and IV are shown in Figures 1 and 2, respectively. We are indebted to Dr.



Fig. 1. Infrared spectra of chlorinated di- and trivinylbenzenes. Upper curve, 1,3-divinyl-2,4,5,6-tetrachlorobenzene; middle curve, 1,4-divinyl-2,3,5,6-tetrachlorobenzene; lower curve, 1,3,5trivinyl-2,4,6-trichlorobenzene.

Philip Sadtler of Samuel P. Sadtler and Son, Inc., for the infrared data. The ultraviolet spectra were determined in Spectro Grade isooctane (2,2,4trimethylpentane) from Phillips Petroleum Company using a Beckman Model DU quartz spectrophotometer. All of the absorptions in the infrared spectra of IV, V, and VI can be assigned to the aromatic system, the vinyl groups or the chlorine substituents. It is of interest that IV and VI, in which all the chlorines are geometrically equivalent, show broad absorption in the 13-14 micron region,



Fig. 2. Ultraviolet spectra of chlorinated di- and trivinylbenzenes. (1) 1,4-Divinyl-2,3,5,6-tetrachlorobenzene; (2) 1,3-divinyl 2,4,5,6-tetrachlorobenzene; (3) 1,3,5-trivinyl-2,4,6trichlorobenzene.

but V, in which the chlorines are not equivalent, gives two absorptions in this region.

In the ultraviolet, both IV and V give a single broad absorption, the former with a maximum at 238 m μ and the latter with a maximum at 230 m μ . This absorption is probably attributable to interaction of the vinyl groups with the aromatic ring. 1,4-Divinyl-2,3,5,6-tetrachlorobenzene, VI,



shows a similar maximum in the 222–232 m μ region, and this, too, is attributable to interaction of the vinyl group with the benzene ring. However, VI gives a second maximum at 261 m μ . This absorption we attribute to an excited state in which structures of the type shown by VII make an appreciable contribution. Such interaction of the vinyl groups is not possible in the case of IV and V where the vinyl groups are meta to one another. As will be shown later, this possibility of interaction of the two vinyl groups in VI has an important bearing on its reactivity.

COPOLYMERIZATION WITH STYRENE

We have studied the copolymerization of styrene with 0.5, 1, and 2% IV at 49.4 \pm 0.1° and 64.8 \pm 0.1° in the presence of 1 and 2 weight per



Fig. 3. Plot of flow time vs. polymerization time for varying percentages of 1,3,5-trivinyl-2,4,6-trichlorobenzene in styrene at 49.4 \pm 0.1°. (1) 2% benzoyl peroxide, 2% IV; (2) 2% benzoyl peroxide, 1% IV; (3) 1% benzoyl peroxide, 2% IV; (4) 2% benzoyl peroxide, 0.5% IV; (5) 2% benzoyl peroxide, 0% IV; (6) 1% benzoyl peroxide, 1% IV; (7) 1% benzoyl peroxide, 0.5% IV; (8) 1% benzoyl peroxide, 0% IV.

cent benzoyl peroxide. The copolymerization reactions were followed by measuring the change in viscosity with time until gelation was approached. At gelation the viscosity of the system is infinite, and the viscosity changes prior to gelation are large. Under these conditions, a rough measure of viscosity is adequate. We have found that the rise of a bubble over a fixed distance in a sealed tube is satisfactory, and, in fact, more reproducible than our previous technique³ of timing the fall of a steel ball through a fixed distance of the polymerization system. The experiments were terminated at or before the gelation point and the systems were analyzed for residual monomeric styrene. The chlorinated monomers do not add bromine under the conditions of the styrene analysis and, thus, do not interfere with the determination of residual styrene.

For a given weight per cent of peroxide catalyst and temperature the

per cent styrene polymerized per hour was constant and independent of the amount of IV present. At $49.4 \pm 0.1^{\circ}$ and 1% benzyl peroxide the per cent styrene polymerized per hour was always 1.08 ± 0.03 ; with 2%benzoyl peroxide, it was 1.53 ± 0.02 . At $64.8 \pm 0.1^{\circ}$ and 1% benzoyl peroxide the per cent styrene polymerized per hour was invariably 4.91 ± 0.05 ; with 2% benzoyl peroxide it was 6.98 ± 0.06 . Under these conditions any increase in viscosity, for a given polymerization time, of a system containing IV over that shown by a system containing only styrene is attribut able to cross-linking of the styrene by IV.

The results at $49.4 \pm 0.1^{\circ}$ with 1 and 2% peroxide are shown in Figure 3 and the results at $64.8 \pm 0.1^{\circ}$ are shown in Figure 4. It is apparent, from



Fig. 4. Plot of flow time vs. polymerization time for varying percentages of 1,3,5-trivinyl-2,4,6-trichlorobenzene in styrene at $64.8 \pm 0.1^{\circ}$. (1) 2% benzoyl peroxide, 2% IV; (2) 2% benzoyl peroxide, 1% IV; (3) 2% benzoyl peroxide, 0% IV; (3) 1% benzoyl peroxide, 0% IV; (5) 1% benzoyl peroxide, 2% IV; (6) 1% benzoyl peroxide, 1% IV; (7) 1% benzoyl peroxide, 0.5% IV; (8) 1% benzoyl peroxide, 0% IV.

these results, that small amounts of IV have an appreciable and controllable affect. Where possible, we have extrapolated our data to infinite viscosity. This permits us to estimate the gelation time and calculate the per cent styrene polymerized at the gelation point. The data are summarized in Table I. In all of the systems we have studied large amounts of styrene have entered the copolymer prior to gelation. However, it is clear that the amount of styrene polymerized at gelation can be varied over even wider limits by changing the polymerization temperature, the concentration of peroxide and/or the concentration of IV.

We have also compared the rate at which IV cross-links styrene with the rates of cross-linking shown by V and VI. The experiments are all at $49.4 \pm 0.1^{\circ}$ with 1 weight per cent benzoyl peroxide and, as before, the amount of styrene polymerized per hour was constant and independent of IV, V and VI. The data for equal weight percentages of the three com-

pounds are shown in Figure 5. Under these conditions, the order of effectiveness is: VI > IV > V. This comparison makes IV appear unduly advantageous since it is trifunctional whereas V and VI are bifunctional. We have also compared the three compounds at equal mole percentages of

TABLE I

Temp., °C.	Wt. % peroxide	Wt. % IV	Gelation time, hours	styrene polymerized at gelation
49.4 ± 0.1	1.0	2.0	36.6	56.0
49.4 ± 0.1	2.0	0.5	36.8	56.4
49.4 ± 0.1	2.0	1.0	35.4	38.2
49.4 ± 0.1	2.0	2.0	31.3	47.9
64.8 ± 0.1	1.0	0.5	12.1	59.5
64.8 ± 0.1	1.0	1.0	11.4	56.0
64.8 ± 0.1	1.0	2.0	10.1	49.5
64.8 ± 0.1	2.0	0.5	9.7	67.7
64.8 ± 0.1	2.0	1.0	9.2	64.2
64.8 ± 0.1	2.0	2.0	8.6	60.0

cross-linking vinyl groups. This corrects for the difference in functionality and gives a more valid comparison. The results are shown in Figure 6. On this basis IV and V are equally effective and VI is considerably more effective than IV and V.



Fig. 5. Effect of various cross-linking agents on the polymerization of styrene at $49.4 \pm 0.1^{\circ}$ with 1% benzoyl peroxide. (1) 1 weight per cent VI; (2) 1 weight per cent IV; (3) 1 weight per cent V; (4) pure styrene.

This result is highly reasonable. In both IV and V the vinyl groups are positioned meta to one another and have a chlorine substituent on each side. Since they are meta to one another, they are incapable of interaction through the aromatic ring. As a first approximation, each vinyl group acts



Fig. 6. Effect of various cross-linking agents on the polymerization of styrene at $49.4 \pm 0.1^{\circ}$ with 1% benzoyl peroxide. Experiments were all run so that 1 mol per cent of the cross-linking vinyl group was present in each case. (1) VI; (2) IV; (3) V; (4) pure styrene.

independently; as a result, at equal mole percentages of the vinyl groups, IV and V would be expected to cross-link styrene at the same rate. Within experimental error, we do in fact observe identical rates of cross-linking.

The ultraviolet absorption spectra offers the basis for a possible explanation of the faster reactivity of 1,4-divinyl-2,3,5,6-tetrachlorobenzene, VI. Consider the addition of a growing chain, $\mathbf{R} \cdot$, to VI. It is possible to write resonance structures for VIII which distribute the odd electron on the α carbon atom to the β -position of the second vinyl group as well as to the ortho and para positions of the aromatic ring. The ultraviolet spectrum of VI indicates that a comparable interaction of the two vinyl groups can make an important contribution to an excited state. It is also probable that, in this case, the stabilization resulting from such interaction is sufficient to appreciably lower the activation energy for addition of a growing chain to the vinyl group and account for the increased rate of cross-linking with VI.



One other effect may also operate to increase the cross-linking effectiveness of VI. The α -positions on IV, V, and VI are all subject to appreciable steric hindrance because of the bulky adjacent chlorine atoms.⁷ With IV and V the product of reaction with a growing chain can add to a monomer molecule only at a hindered α -position. With VI it is at least conceivable that the interaction of the vinyl groups discussed above would make it possible for VIII to add to a monomer molecule at the unhindered β -position of the second vinyl group because of the contribution from IX.



We also tried to compare the commercially available mixed divinylbenzenes with the cross-linking agents discussed above. Our results were vitiated by the incursion of popcorn formation at our conditions of temperature and concentration. One experiment at the concentrations and temperature of Figure 6 would indicate that the divinylbenzenes cross-link styrene much more rapidly than IV, V, and VI. In this particular experiment the first measurable increase in viscosity was noted at 10.5 hours, and at 11 hours the viscosity was infinite. This experiment, with only 0.5 mole per cent of divinylbenzene present, gave 12% polymerization at gelation.

EXPERIMENTAL

Eastman Kodak Co. white label styrene was extracted two times with 10% aqueous sodium hydroxide, washed with water, dried over magnesium sulfate and distilled at reduced pressure. The styrene was used immediately after distillation. 1,3,5-Trivinyl-2,4,6-trichlorobenzene, IV, was crystallized from methanol-ether to a constant m.p. of 64-65°; V was crystallized from methanol to a constant m.p. of 86°. Eastman Kodak Co. benzoyl peroxide was crystallized from chloroform-methanol.

The copolymerization measurements were made as follows: Solutions were prepared by dissolving the requisite quantities of benzoyl peroxide and the cross-linking agent in styrene. The solutions were placed in 13 mm. O.D. tubes, which had a mark about the tubes 5" from the bottom and a constriction 8" from the bottom. The tubes were filled to a point exactly 6" from the bottom. Air was removed by two cycles of freezing in dry ice-trichloroethylene, evacuating on the water pump, thawing, and flushing with dry oxygen-free nitrogen. The tubes were then sealed at the constrictions under 200-250 mm. nitrogen pressure. Flow times were determined by holding the tube with the sealed end down, flipping the tube over and determining the time required for the top of the bubble to each the 5" mark. The flow time was plotted against the reaction time, and the gelation point was taken as that at which the curve approached the vertical. This corresponds to the point at which the viscosity of the system approaches infinity.

Tubes were removed from the thermostat at or before the gelation time and frozen in dry ice until they could be opened for analysis. Weighed samples were dissolved in carbon tetrachloride and analyzed for residual styrene by the standard bromide-bromate titration.

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Synopsis

1,3,5-Trivinyl-2,4,6-trichlorobenzene has been prepared and its copolymerization, at low weight percentages, with styrene has been studied by following the change in viscosity of the polymerizing system as a function of time. The copolymerization was studied as a function of the concentration of the trivinyl compound (0.5-2 weight per cent) at two temperatures and two benzoyl peroxide concentrations. The gelation times and per cent styrene polymerized at gelation were estimated. In addition, the copolymerization of 1,3,5-trivinyl-2,4,6-trichlorobenzene with styrene was compared with that of 1,4-divinyl-2,3,5,6-tetrachlorobenzene and 1,3-divinyl-2,4,5,6-tetrachlorobenzene, both with styrene. The infrared and ultraviolet spectra of the three cross-linking agents were determined. The ultraviolet spectrum of 1,4-divinyl-2,3,5,6-tetrachlorobenzene provides a basis for explaining its greater reactivity in copolymerization with styrene.

Résumé

Le 1.3.5-trivinyl-2.4.6-trichlorobenzène a été préparé et sa copolymérisation à de faibles pourcentages avec le styrène a été étudiée en suivant la variation de viscosité du système en polymérisation en fonction du temps. La copolymérisation a été étudiée en fonction de la concentration en composé trivinylique (0.5 à 2% en poids) à deux températures et à deux concentrations en peroxyde de benzoyle. Les temps de gélification et le pourcentage de styrène polymérisé au point de gélification ont été estimés. En outre, la copolymérisation du 1.3.5-trivinyl-2.4.6-trichlorobenzène avec le styrène a été compàrée avec la copolymérisation du 1.4-divinyl-2.3.5.6-tétrachlorobenzène et celle du 1.3-divinyl-2.4.5.6-tétrachlorobenzène avec le styrène également. Les spectres infrarouges et dans l'ultraviolet de ces trois agents de pontage ont été déterminés. Le spectre ultraviolet du 1.4-divinyl-2.3.5.6-tétrachlorobenzène permet d'expliquer sa réactivité plus considérable dans sa copolymérisation avec le styrène.

Zusammenfassung

1,3,5-Trivinyl-2,4,6-trichlorbenzol wurde hergestellt, und seine Copolymerisation bei niedrigen Gewichtsprozenten mit Styrol wurde durch Messen der Viskositätsänderung im Polymerisationssystem als Funktion der Zeit untersucht. Die Copolymerisation wurde als Funktion der Konzentration der Trivinylverbindung (0,5-2 Gewichtsprozent) bei zwei Temperaturen und zwei Benzoylperoxydkonzentrationen untersucht. Die Gelierungszeiten und die bei Gelierung polymerisierten Prozente Styrol wurden abgeschätzt. Ausserdem wurde die Copolymerisation von 1,3,5-Trivinyl-2,4,6-trichlorbenzol mit Styrol mit der von 1,4-Divinyl-2,3,5,6-tetrachlorbenzol und 1,3-Divinyl-2,4,5,6tetrachlorbenzol, beide mit Styrol, verglichen. Die infraroten und ultravioletten Spektra der drei Querbindungsmittel wurden bestimmt. Das ultraviolette Spektrum von 1,4-Divinyl-2,3,5,6-tetrachlorbenzol gibt eine Grundlage zur Erklärung seiner grösseren Reaktionsfähigkeit bei Copolymerisation mit Styrol.

Received January 24, 1952