2,5-Bis(trifluoromethyl)-3,4-dichlorothiophene (VIII).—IX (27.5 g.) was added to excess silver fluoride (90 g.) and heated in an oil bath. At 115°, a smooth reaction started which was completed at 150°. Distillation *in vacuo* and rectification by using a Widmer column yielded VIII (13.2 g., 54%); b.p. 46–50° (7 mm.); b.p. 173–174° (760 mm.); $n^{27}\text{D}$ 1.4402.

Anal. Calcd. for $C_6Cl_2F_6S$: C, 24.93; Cl, 24.53; F, 39.44. Found: C, 24.72, 24.83; Cl, 24.72, 24.44; F, 39.22, 39.00.

The same product VIII (4.2 g., 43%) was obtained from VI (13 g.) and excess silver fluoride (60 g.) upon heating in an oil bath; $n^{15}\text{D}$ 1.4438.

1,1,1,2,5,6,6,6-Octafluoro-3,4-dichlorohexadiene-3,4 (X).—VIII (4.5 g.) was added to silver difluoride (10 g.) and heated in an oil bath. At 93°, the reaction started and became vigorously with evolution of white fumes at 130°. The temperature was maintained for several minutes and, after cooling, the liquid reaction product was distilled from the silver salts. Fractionation yielded X (1.4 g., 33%); b.p. 122–124°; $n^{21}\text{D}$ 1.3558.

Anal. Calcd. for $C_6Cl_2F_8$: C, 24.42; F, 51.52. Found: C, 24.13, 24.33; F, 53.00, 53.37; S, traces (qualitative chlorine test was positive).

Acknowledgment.—We are very much indebted to the Olin Mathieson Chemical Corporation, New York, N. Y., for the generous support of this work and to Dr. H. Agahigian, Central Analytical Department, Olin Mathieson Chem. Corp., for the evaluation of the NMR spectra.

The Preparation and Polymerization of *p*-Vinylbenzyl Ethers

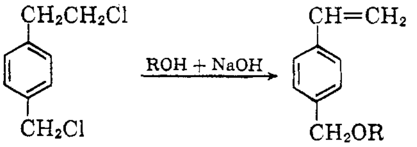
EARL C. CHAPIN,[1] JOHN G. ABRAMO, AND VIRGINIA L. LYONS

Monsanto Chemical Company, Plastics Division, Springfield, Mass.

Received January 19, 1962

p-Vinylbenzyl ethers were prepared by the action of alcoholic base on *p*-(β-chloroethyl)benzyl chloride. The reaction proceeded successfully for normal and secondary alcohols, but tertiary alcohols and phenols did not give the desired product. These ethers were polymerized to give products which were soft and extensible at room temperature when the ether group was larger than butyl. Normal alkyl or alkoxyethyl ethers gave polymers having a gradual reduction in glass temperature as the length of the substituent group was increased. Polymers from the branched ethers and those containing a terminal hydroxyl on the substituent group gave glass temperatures well above the corresponding *n*-alkyl ethers. By comparison of the glass temperatures of the *p*-vinylbenzyl *n*-alkyl and ethoxyalkyl ethers with those of *p*-*n*-alkylstyrenes it was found that these values depend only on the number of atoms in the substituent group on the benzene ring and not on whether these atoms are carbon or oxygen.

When *p*-(β-chloroethyl)benzyl chloride[2] was allowed to react with an alkali metal hydroxide in an alcohol, the product was the corresponding *p*-vinylbenzyl ether. Nucleophilic replacement of the benzyl chlorine and dehydrohalogenation occurred in a single reaction step:



The reaction proceeded smoothly and in good yield. Polymerization in the final distillation step complicated recovery of the product and precluded careful fractionation of all but the lowest members of the series. Phenylenediamine and diphenylpicrylhydrazine were the best inhibitors found for this distillation. Hydroquinone proved to be too volatile especially in the case of the higher boiling members and sulfur gave contamination of the distilled monomer which interfered with subsequent polymerization steps.

All primary and secondary alcohols gave the desired product. *t*-Butyl alcohol gave a sluggish reaction and no *t*-butyl ether was obtained. Instead some impure *p*-vinylbenzyl alcohol and a small yield of a crystalline compound, m.p. 60°, tentatively identified as 4,4′-divinyldibenzyl ether were the only products isolated. Phenol did not give the expected *p*-vinylbenzyl phenyl ether but led to much more complicated products which were not identified. The only *p*-vinylbenzyl ether previously reported was the optically active *sec*-butyl ether by Marvel and Overberger.[3]

The *p*-vinylbenzyl ethers were polymerized in solution at 120° using di-*t*-butyl peroxide as initiator. Toluene or methanol was used as a solvent. The polymerization conditions used were chosen such that approximately a 60–85% conversion was obtained. These conditions were chosen to minimize gelation of the polymer which results when the polymerization is allowed to proceed to higher conversion or run at lower temperatures. We believe this tendency to cross-linking is due to extensive chain transfer at the benzyl hydrogen sites in the monomer and polymer. Cross-linking by chain transfer to polymer has been reported for other monomers such as methyl acrylate or vinyl acetate.[4]

---

(1) Address inquiries concerning this paper to the above at Western New England College, Springfield 9, Massachusetts.

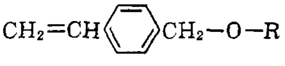
(2) J. G. Abramo and E. C. Chapin, *J. Org. Chem.*, **26**, 2671 (1961).

(3) C. S. Marvel and O. G. Overberger, *J. Am. Chem. Soc.*, **66**, 475 (1944).

(4) T. G. Fox and S. Gratch, *Ann. N. Y. Acad. Sci.*, **57**, 367 (1953).

TABLE I

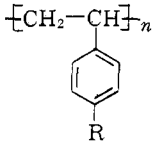
p-VINYLBENZYL ETHER MONOMERS



R	B.p., °C.	% Conversion to monomer	Refractive index at 25°	Found C	Found H	Calcd. C	Calcd. H
Methyl	44 (0.2 mm.)	68.5	1.5378				
n-Propyl	55–58 (0.1 mm.)	67	1.5224	81.03 81.05	9.18 9.02	81.77	9.15
n-Butyl	82–87 (0.1 mm.)	59.5	1.5166	81.14 81.26	9.38 9.28	82.06	9.54
sec-Butyl	78–84 (0.35–0.45 mm.)	66	1.5189	81.44 81.71	9.44 9.24	82.06	9.54
n-Hexyl	94–100 (0.06 mm.)	77.7	1.5100	82.59 82.67	10.33 10.31	82.51	10.16
n-Octyl	117–124 (0.25 mm.)	54.5	1.5040	82.72 82.74	10.77 10.55	82.86	10.64
2-Ethylhexyl	116–117 (0.35–0.4 mm.)	38.6	1.5285			82.86	10.64
Ethoxyethyl	98–103 (0.4 mm.)	44	1.5199	75.06 75.19	8.89 8.91	75.69	8.80
Butoxyethyl	110 (0.1 mm.)	53.5	1.5090	76.36 76.64	9.46 9.31	76.88	9.46
Hydroxyethyl	104–110 (0.25 mm.)	68.4	1.5519	73.92 74.13	8.11 7.93	74.13	7.92
Hydroxybutyl	120–128 (0.4 mm.)	39	1.5323	74.79 74.90	8.85 8.94	75.68	8.74

TABLE II

INTRINSIC VISCOSITY AND GLASS TEMPERATURE OF THE POLY-p-VINYLBENZYL ETHERS AND p-n-ALKYLSTYRENES



R	$[\eta]$,[a] dl./g.	Tg, °C.
$-CH_2CH_3$	0.52	78[b]
$-CH_2OCH_3$	.65	77
$-CH_2CH_2CH_2CH_3$	.49	48
$-CH_2OCH_2CH_2OH$	.66[c]	46
$-CH_2OCH_2CH_2CH_3$	.50[c]	22
$-CH_2OCH_2CH_2CH_2CH_3$	.57	10
$-CH_2O\overset{CH_3}{\overset{\vert}{C}}HCH_2CH_3$	.48	40
$-CH_2OCH_2CH_2CH_2CH_2OH$	.68[d]	20
$-CH_2OCH_2CH_2OCH_2CH_3$	.43	0
$-CH_2OCH_2CH_2CH_2CH_2CH_2CH_3$	.52[e]	−20
$-CH_2O\overset{CH_2CH_3}{\overset{\vert}{C}}HCH_2CH_2CH_2CH_2CH_3$	.6	−23
$-CH_2OCH_2CH_2OCH_2CH_2CH_2CH_3$	.61	−38
$-CH_2OCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	.64	−42

[a] Toluene was used as solvent unless otherwise noted. [b] Determined dilatometrically. [c] Intrinsic viscosity was 1.15 dl./g. after storage for one year. [d] Pyridine was used as solvent. [e] Intrinsic viscosity was 1.62 dl./g. after storage for one year.

The polymers were carefully purified by precipitation and leaching with methanol or hexane. Care was exercised to assure that the polymer samples taken for testing were free from unpolymerized monomer and solvent. An antioxidant, t-butyl-p-cresol, was added to the precipitant to prevent cross-linking of the samples on storage. Even with this precaution the viscosity of the polymers increased markedly on storage (see Table II).

The dynamic properties of these polymers were determined using the torsion pendulum as described by Nielsen.[5] The point of maximum damping on the plot of damping *vs.* temperature was taken as the glass temperature. These values along with the intrinsic viscosity of the polymers are shown in Table II.

It was found that the glass temperature (T_g) of the poly-p-vinylbenzyl n-alkyl and alkoxyethyl ethers decreased as the length of the substituent group increased (Fig. 1). The T_g values for the poly-p-vinylbenzyl ethers having branched substituent groups were about 20–30° higher than those for the polymers from the corresponding straight chain compounds. The polyvinylbenzyl ethers having substituent groups terminating in hydroxyl also gave higher values than were obtained on polymers having the same length of nonpolar substituent.

Since the data for the polymers having n-alkyl and alkoxyethyl substituents are in close agreement, we concluded that an oxygen atom in the side chain has essentially the same effect as an additional methylene group. We would, therefore, expect that the benzyl ether oxygen would also have no particular effect on glass temperature except that of lengthening the substituent chain by an additional unit. The glass temperatures of poly-p-(n-alkyl)styrenes should therefore be comparable to the poly-p-vinylbenzyl n-alkyl ethers for the same length of side chain. The glass temperatures for a series of poly-p-(n-alkyl)styrenes have been reported by Overberger, Frazier,

---

[5] L. E. Nielsen, *Rev. Sci. Instr.*, **22**, 690 (1951).

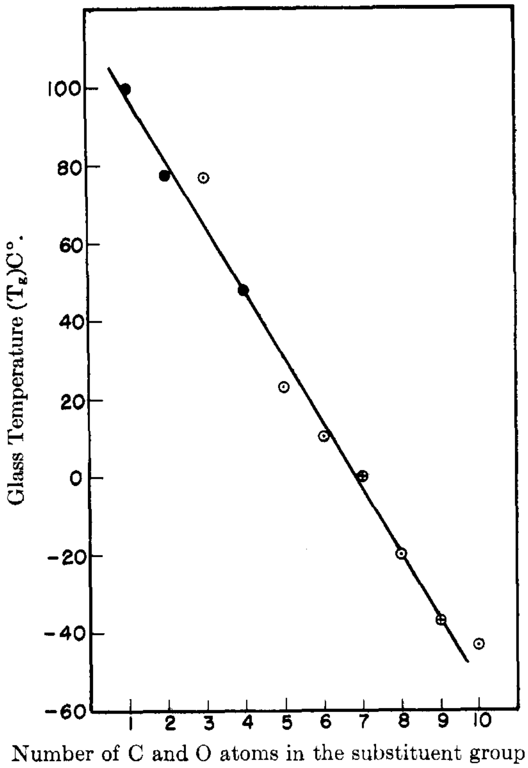


Fig. 1.—Glass temperature *vs.* length of a substituent group in the *para* position of polystyrenes: ⊙, poly-*p*-vinylbenzyl *n*-alkyl ethers; ⊕, poly-*p*-vinylbenzyl ethoxyethyl and butoxyethyl ethers; ●, poly-*p*-methyl-, *p*-ethyl- and *p*-butylstyrene.

Mandelman, and Smith.[6] Their values are very low and do not agree with the values obtained here on the poly-*p*-vinylbenzyl ethers.

We have also prepared samples of *p*-ethyl- and *p*-butylstyrene by the methods reported.[6] Careful infrared and vapor phase chromatographic analysis showed that these samples contained only the *para* isomer. The monomers were polymerized and the polymers carefully purified. The glass temperature of these polymers are shown in Table II. The value of 100° for the T_g of *p*-methylstyrene was taken from the data of Barb.[7] These newer values are in reasonably close agreement with the values obtained for the poly-*p*-vinylbenzyl ethers.

Experimental

Monomer Preparation.—All of the *p*-vinylbenzyl ethers (Table I) were prepared by the general method described below. A solution of the alcohol (500 ml.), sodium hydroxide (80 g., 2 moles), and a trace of hydroquinone was heated to 120°. *p*-(β-Chloroethyl)benzyl chloride (62 g., 0.33 mole) was then added dropwise to the hot alcoholic base maintaining the temperature at 120°. This addition required about 30 min. and the reaction mixture was heated an additional hour at 120°. The cooled reaction mixture was added to water and extracted with benzene. The benzene layer was dried with anhydrous magnesium sulfate and distilled using phenylenediamine or diphenyl picrylhydrazine as inhibitor.

Attempt to Prepare *p*-Vinylbenzyl-*t*-butyl Ether.—When the procedure described above was carried out using *t*-butyl alcohol and potassium hydroxide, 6.1 g. of liquid, b.p. 73–80° at 0.3 mm. was obtained. This was shown to be impure *p*-vinylbenzyl alcohol by comparison with an authentic sample. The remaining isolable product, 10 g., melted at 60° after recrystallization from methanol.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.05; 85.98; H, 7.47, 7.62.

Polymerization.—The *p*-vinylbenzyl ether monomer was dissolved in a solution of 0.2 ml. di-*t*-butyl peroxide in 100 ml. of toluene to make a 30 mole % solution. This solution was charged to a 300-ml. capacity pressure bomb and heated under nitrogen at 120° ± 2° for about 20 hr. The viscous polymer solution was diluted with benzene and the polymer precipitated in methanol. The polymers were leached for several days in methanol containing a trace of *t*-butyl-*p*-cresol. The *p*-vinylbenzyl hydroxyethyl ether, ethoxyethyl ether, and hydroxybutyl ether were polymerized in ethanol since these polymers were found to be insoluble in toluene. These polymers were precipitated in hexane and leached in hexane to purify them. The polymers were dried for 24 hr. *in vacuo* at room temperature.

Specimen Preparation.—Test specimens of these polymers were prepared by compression molding. The softer samples in which R>butyl were slightly crosslinked during the molding by applying a small amount of di-*t*-butyl peroxide to the polymer surface. Samples that were not treated in this manner did not cross-link. Molding temperatures of about 150° were used and the samples were cooled slowly to relieve strains in the samples. Teflon sheets were used over the platens of the mold to prevent sticking and the samples were dusted with sodium bicarbonate to allow handling.

Acknowledgment.—The authors wish to thank Dr. Seymour Newman for his help in the determination and interpretation of the glass temperatures reported and Mr. Q. A. Trementozzi for his helpful advice and encouragement.

---

[6] O. G. Overberger, C. Frazier, J. Mandelman, and H. F. Smith, *J. Am. Chem. Soc.*, **75**, 3326 (1953).

[7] W. G. Barb, *J. Poly. Sci.*, **37**, 515 (1959).