

Isobutylene Copolymers of Vinylbenzyl Chloride and Isopropenylbenzyl Chloride

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The cationic copolymerization of isobutylene with styrene^{4,5,13} and α -methylstyrene² is known. Leary⁴ emphasizes the need for a continuous feed and constant conversion copolymerization to overcome the tendency of the isobutylene to enter the copolymer faster than the styrene. The data of Leary⁴ and Tegge¹³ indicate an r_1 (for styrene) of 0.6 ± 0.3 and an r_2 (for isobutylene) of 3 ± 1 , and that of Medvedev and co-workers⁵, and r_1 of 0.17 and r_2 of 1.60. Medvedev and co-workers also have reported styrene- α -methylstyrene r_1 and r_2 values which indicate that α -methylstyrene would be more reactive than isobutylene.

In the present work with ethyl chloride as solvent and boron trifluoride as the catalyst, the r_1 , r_2 values found for isobutylene and the styrene derivatives are in general agreement with these data. The values for vinylbenzyl chloride (M_1) and isobutylene (M_2) were found to be 0.7 ± 0.1 and 4.5 ± 1 . The values for isopropenylbenzyl chloride (M_1) and isobutylene (M_2) were on the order of 1 and 0.4. Some copolymerizations were carried out with vinylbenzyl chloride (M_1) and propylene (M_2), and values of $r_1 > 1$ and $r_2 < 1$ were indicated.

Overberger⁹ had reported that isobutylene copolymerized regularly with *p*-chlorostyrene in a hydrocarbon solvent, but we did not observe any decrease in disproportionation when hexane was used in place of ethyl chloride.

The copolymers prepared were further treated with nucleophilic reagents in order to enhance tensile strength and other rubberlike properties, to incorporate sites for grafting, and to obtain material that could be cast into semipermeable membranes.

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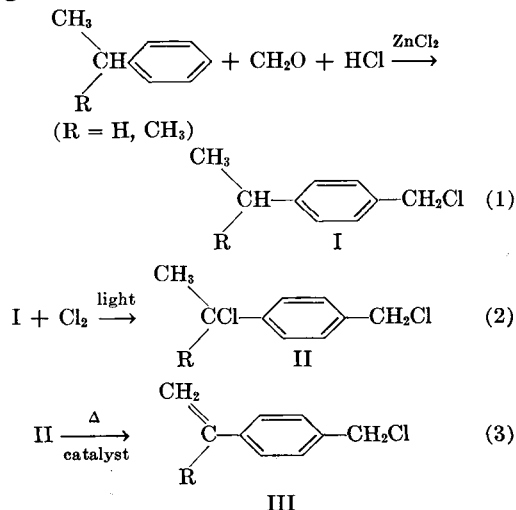
EXPERIMENTAL

Materials

Boron trifluoride was used as supplied by Matheson. It was transferred by means of a gas buret, with mercury as the confining liquid. Ethyl chloride, Dow U.S.P. grade, was vaporized from its cylinder through drying towers and condensed in a Dry Ice trap. The trap was sealed off and weighed before the ethyl chloride was transferred to the reactor as a liquid by displacement with dry nitrogen. Isobutylene or propylene (Matheson, C.P.) was dried and transferred in the same manner as the ethyl chloride.

Preparation of Monomers

Vinylbenzyl chloride was prepared as shown in eqs. (1), (2), and (3) by the method of McMaster and Stowe,⁷ and was a mixture of *para* and 30-40% *ortho* isomers. A few copolymerizations were carried out with the pure *para* isomer which had been obtained by fractional distillation and freezing.



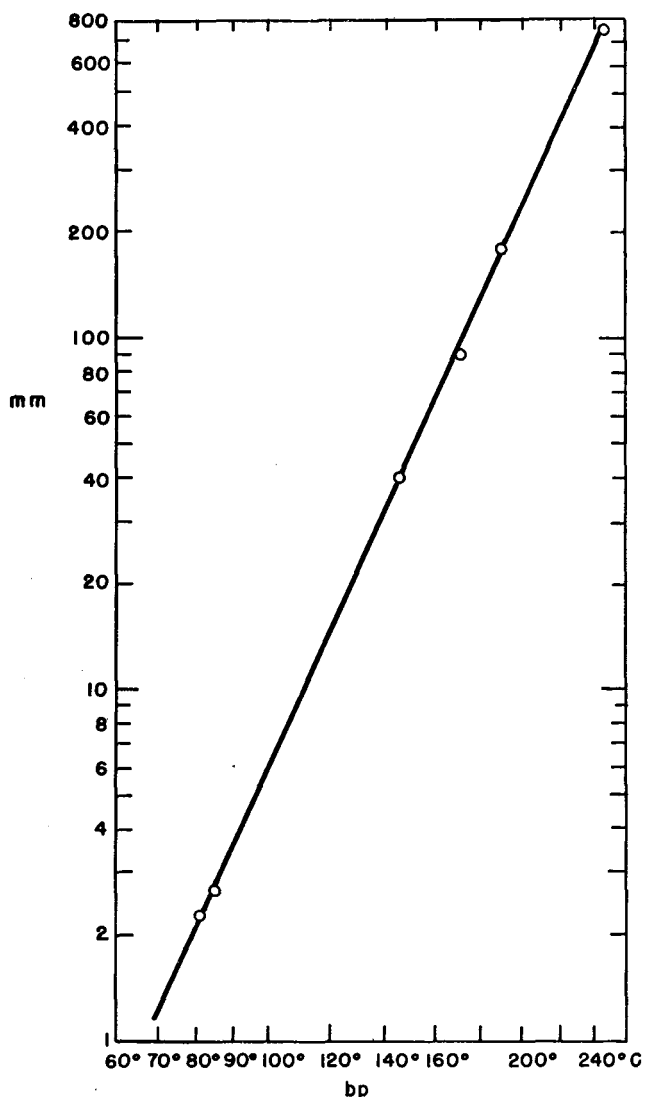


Fig. 2. Physical constants for isopropenylbenzyl chloride, $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$: freezing point, 27.39°C .; n_D^{30} , 1.5600; d^{30} , 1.0573.

activities of primary, secondary, and tertiary hydrogens in chlorination and other free-radical reactions, as well as studies of the effects of other substituents on these reactivities. Table I shows the relative reactivities of primary, secondary, and tertiary sites in toluene, *tert*-butylbenzene, and cumene, determined by Walling in competitive chlorination experiments.¹⁵ The first column shows the number of moles that are chlorinated in the time it takes to chlorinate one mole of toluene. From these data, the second column is calculated by combining and applying appropriate weighting. From these data, one would predict that the first chlorine entering isopropyltoluene would be found in the α , β , and α' positions in the

TABLE I
Relative Reactivities of Primary, Secondary, and Tertiary Sites on Substituted Aromatics^a

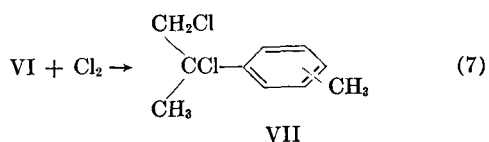
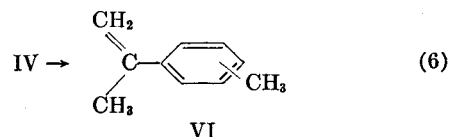
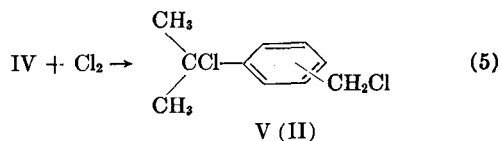
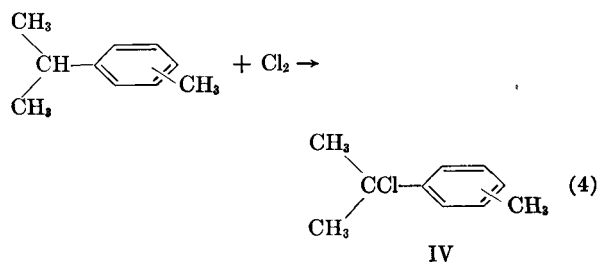
	Reactivity per molecule	Reactivity per hydrogen
$\begin{array}{c} \text{CH}_3 \\ \\ \text{HC}-\text{Ar} \end{array}$ (cumene)	2.8	6.84
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{Ar} \end{array}$ (<i>tert</i> -butylbenzene)	0.315	0.105
$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}-\text{Ar} \\ \\ \text{H} \\ \\ \text{H} \end{array}$ (ethylbenzene)	2.30	3.18 ^b
CH_3-Ar (toluene)	1.00	1.00

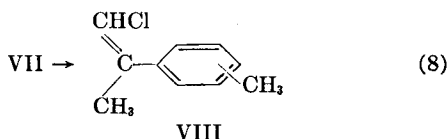
^a Data of Walling and Jacknow.¹⁵

^b α -Hydrogen only.

ratio 2.59:0.21:1.00. The published data provide an insufficient basis for predicting the distribution of second chlorines, but if one assumes the same relative reactivities and no dichlorinated carbons, the ratio of α, α' -disubstituted to any β -substituted molecules should be about 2.98:0.82.

We had hoped to prepare α, α' -dichloroisopropyltoluene by the direct chlorination of cymene, as in eqs. (4) and (5), but our experience





indicated that dehydrochlorination, equation (6), was promoted by the conditions of the chlorination, leading to the formation of α,β -dichloroisopropyltoluene (VII), β -chloroisopropenyltoluene (VIII), etc. We were able to obtain only very small yields of *p*-isopropenylbenzyl chloride from *p*-cymene by this route. With *o*- and *m*-cymene, yields were negligible.

Vinylbenzyl dimethylamine

To a solution of 650 ml. 25% aqueous dimethylamine in 200 ml. dioxane was gradually added 100 ml. vinylbenzyl chloride with agitation. After the mixture had stood for two days the calculated amount of potassium hydroxide was added. The aqueous layer was extracted with ether. The extract was combined with the organic layer and fractionally distilled in a Vigreux column. The yield was 86 g. (74.8%), b.p. 81–85.5°C. at 5 mm. The product was 90% *para*, 10% *ortho*. The boiling point reported¹⁴ for the *ortho* isomer is 102°C. at 17 mm.

The purity found by unsaturation titration (bromate–bromide) was 93.3%. A 0.01% iso-octane solution of the monomer had absorption peaks at 278 and 294 $m\mu$. By analysis the nitrogen content was found to be 8.18%, equivalent to 94% purity.

A sample which was 98.4% pure by unsaturation analysis boiled at 81–83.5°C. (5 mm.). The boiling point of the pure material is considered to be 82.5 to 83.0°C. at this pressure.

Copolymerizations

The polymerizations were carried out in a 1-l. stirred glass reactor cooled with liquid nitrogen and ethyl chloride. All equipment was flushed for several hours with dry, oxygen-free nitrogen before use, and a slow stream of nitrogen was passed into the reactor during polymerizations to prevent the entrance of moisture.

The styrene derivative was washed with caustic to remove inhibitor, and dried over calcium chloride.

Boron trifluoride was added either above or below the liquid surface a few milliliters at a time. After an induction period of variable length (depending on the amounts of residual moisture

present) the effect of each addition of boron trifluoride could be noted as a temperature rise.

In experiment 35B, 71 g. isobutylene and 6.5 g. isopropenylbenzyl chloride (98% pure) were dissolved in 321 g. ethyl chloride. To this solution, chilled to -105°C . in a liquid nitrogen–ethyl chloride bath, was added 16 cc. boron trifluoride gas. After 10 min. another 22 cc. boron trifluoride was added and then rapid polymerization occurred. The temperature rose to -100°C . in 10 sec. The short stop (aqueous acetone) was injected at this time, but the temperature rose to -96°C . before the reaction stopped. A yield of 31.5 g. of rubbery polymer was obtained after three reprecipitations in methanol from toluene solution. The viscosity of a 10 wt.-% solution of the copolymer in toluene was 56.1 cpoise. The polymer contained 3.04% chlorine or 5.3 mole-% as compared to 3 mole-% in the feed. The combined liquors from the precipitations were titrated by bromate–bromide and were found to contain 2.0 g. unpolymerized *p*-isopropenylbenzyl chloride. The amount copolymerized was 4.5 g. according to the chlorine analysis and yield; therefore, all the *p*-isopropenylbenzyl chloride was accounted for.

In experiments used for rate calculations, the temperature was held within ten degrees of the indicated temperature. In a few experiments,

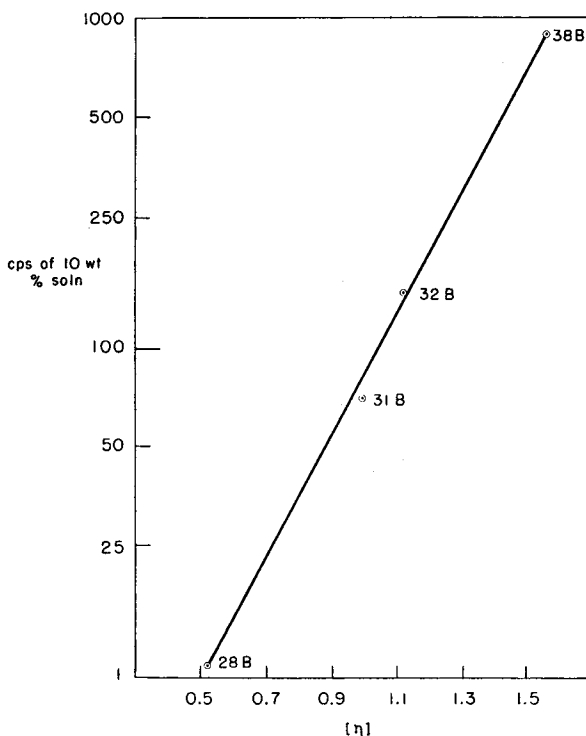


Fig. 3. Relationship of concentrated and dilute solution viscosity in toluene (copolymers low in styrene derivative).

runaway reactions occurred in which the temperature rose as much as fifty degrees before a short-stop could be added. The product for such a run was used for further experiments, but the conversion was too high to permit the use of such data in calculations of r_1 and r_2 .

For purposes of comparison, Figure 3 shows the relationship between the viscosities of 10 wt.-% solutions in toluene and the intrinsic viscosities $[\eta]$ of several samples.

RESULTS AND DISCUSSION

In order to obtain samples of approximately even composition, it was necessary to stop reactions at low conversion. Table II shows data for low-conversion runs with vinylbenzyl chloride. These data were used for the calculation of r_1 and r_2 values by the method of Mayo and Walling.⁶ The resulting plot is shown in Figure 4. Table III shows data from several copolymerizations with vinylbenzyl chloride that were carried to higher conversion. It had been anticipated that in the presence of a Friedel-Crafts catalyst such as boron trifluoride, the reactive benzylic chlorine might alkylate either the monomers or the chain, which would result in crosslinking or in secondary chlorines that would not aminate. We had no evidence of such reactions at the low temperatures used for polymerization. Some samples in fact, were observed to become insoluble when heated, for example in molding, but this may have been due to incorporation of traces of other Friedel-Crafts catalysts in the samples. (Wohl and Wertyporoch,¹⁶ Burwell and Archer,¹ and, in the past year, Russell¹¹ have reported that boron trifluoride will not catalyze the alkylation of benzene by alkyl chlorides.) On the other hand, in experiment 15B, AlCl_3 was used, and as expected about half of the product was insoluble.

Table IV shows data obtained with isopropenyl-

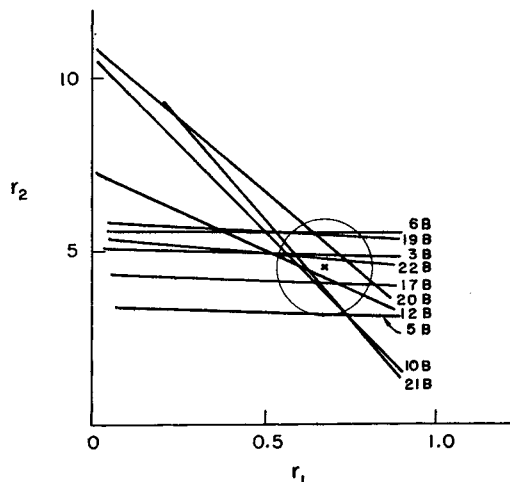


Fig. 4. Plot for r_1 , r_2 for vinylbenzyl chloride (M_1) and isobutylene (M_2) copolymerization.

benzyl chloride. In this case, the polymer is richer than the feed in the chlorine-containing monomer. The exceptions, runs 30 and 31 which were carried to high conversion, are not explained.

Since the polymer composition was determined by chloride determinations, any loss of chlorine from hydrolysis or other reaction would have led to

TABLE III
High-Conversion Copolymerization of
Vinylbenzyl Chloride (M_1) with Isobutylene
Solvent: Ethyl Chloride; Catalyst: BF_3

Expt. no.	Temp., °C.	Conversion, %	[M_1], mole-%		Viscosity, cpoise
			Monomer	Polymer	
7B	-60	45	6.9	0.6	18
11B	-60	53	16.5	3.5	10
41B	-100	36	6.9	1.5	20
10B	-60	64	10.7	1.4	34
9B	-60	70	16.6	5.2	30
15B*	-45	{27 36}	15.6	{12.2 6.9}	Insol. 2

* With AlCl_3 as catalyst.

TABLE II
Low-Conversion Copolymerization of
Vinylbenzyl Chloride (M_1) with Isobutylene
Solvent: Ethyl Chloride; Catalyst: BF_3

Expt. no.	Temp., °C.	Conversion, %	[M_1], mole-%		Viscosity, cpoise
			Monomer	Polymer	
17B	-70	23	5.3	1.5	31
12B	-115	13	9.0	1.6	107
43B	-100	11	9.5	1.7	22
20B	-80	8	11.6	1.2	32
22B	-110	8	22.1	6.4	148
21B	-80	4	29.4	7.2	45
45B	-103	7	34.6	14.9	—

TABLE IV
Copolymerization of Isopropenylbenzyl Chloride (M_1) with
Isobutylene
Solvent: Ethyl Chloride; Catalyst: BF_3

Expt. no.	Temp., °C.	Conversion, %	[M_1], mole-%		Viscosity, cpoise
			Monomer	Polymer	
32B	-110	53	0.9	1.3	148
35B	-100	41	3.0	5.3	56
44B	-100	64	6.1	9.1	15
47	-102	11	7.7	8.5	22
30B	-122, -105	92	4.6	3.8	44
31B	-125, -93	98	2.4	1.7	71

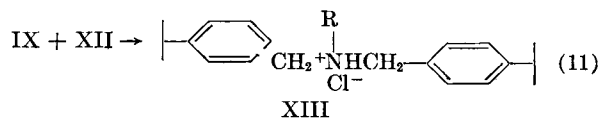
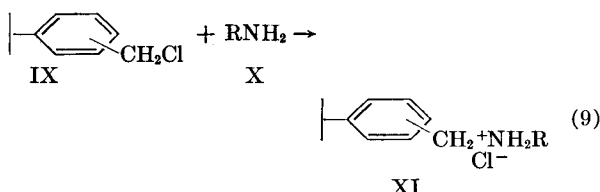
low values for the styrene derivative. The fact that at very high conversion the polymer composition did not agree as it should have with the starting composition suggested that such reactions might have taken place to some extent. In the test case 7B, however, it was found that C, H, and Cl analyses added up to 100.18%, and therefore hydrolysis was discounted. This same copolymer was examined by ultraviolet absorption spectroscopy and was found to contain 1.8 wt.-% of the polyvinylbenzyl chloride groups. Chloride analysis showed 1.72 wt.-% benzyl chloride. In another experiment (35B) the chlorine in the copolymer and the unreacted monomer recovered from the methanol-toluene solution accounted for all of the isopropenylbenzyl chloride in starting mixture.

Reactive Sites in the Copolymers

The benzylic chlorine provides a site for further reaction with a variety of nucleophilic reagents. Thus these copolymers can be aminated or otherwise substituted in order to impart special properties. Crosslinking can be accomplished by various means. The ease of crosslinking and the properties imparted depend on the amount of benzylic chlorine in the copolymer, the molecular weight, and the crosslinking agent chosen. Copolymers containing as little as 0.8 mole-% chlorine were crosslinked to insoluble polymers. Ammonia, and methyl-, ethyl-, and propylamine, reacted to crosslink chlorine-containing polymers even when present in excess. Higher monoamines failed to do so at a detectable rate, probably because of the decrease in nucleophilicity caused by the increasing steric hindrance of the product first formed.

In one experiment with copolymer 11B (2.08 wt.-% chlorine), benzylamine was used as the aminating agent. While there was no evidence of crosslinking, benzylammonium chloride and a nitrogen-containing polymer were formed. Elementary analysis of the reprecipitated polymer showed 0.87% nitrogen (a value of 0.82% was calculated from the original chlorine content).

The crosslinking by amines occurs as shown in the following reactions:



Whether the crosslinking reaction (11) takes place depends both on the basicity of the product first formed (XI) compared with that of the starting reagent (X), and on the nucleophilicity of this secondary benzylamine (XII).

It is one thing to produce a crosslinked or insoluble material, another to produce a useful rubber. Unless the viscosity of the copolymer was at least 100 cpoise, the strength was not very high with or without curing. The data of Table V do, however, show that crosslinking and strengthening were taking place, that there is an optimum amount of curing agent, and that there is considerable difference between similar curing agents.

Diethylenetriamine was not as effective a crosslinking agent as had been expected; it may be that the first reaction occurred on the middle nitrogen, after which the nucleophilicity of the remaining nitrogens was reduced by their proximity to the positive charge. On an equimolar basis, 3,3'-diaminodipropylamine was more reactive than either diethylenetriamine or decamethylenediamine. Decamethylenediamine was compared with 3,3'-diaminodipropylamine as a curing agent by observing the viscosity rises in solutions of the treated copolymer. An isopropenylbenzyl chloride copolymer, 31B, having 1.7 mole-% chloride and viscosity of 71 cpoise was used. A 5% solution in toluene was treated with the equivalent amount of amine (assuming that only two of the three nitrogens in the triamine would react). After two days of heating at 70°C. the viscosity of the solution containing the triamine had risen 85% and that with the diamine 12%. Amination of an isobutylene-vinylbenzyl chloride copolymer containing 0.49% chlorine was carried out at 110°C. by immersion of a film for

TABLE V
Properties of Amine-Cured Unreinforced Polymer^a

Curing agent	$\frac{[-\text{NH}_2]^b}{[-\text{Cl}]}$	Tensile strength, psi	Elongation, %
3,3'-Diaminodipropylamine	0.3	154	626
	0.5	384	324
	1.0	237	86
Diethylenetriamine	0.3	56	863
	0.5	21	879
	1+	290	215

^a Polymer Sample 9B, 5.17 mole-% vinylbenzyl chloride, viscosity 29.46 cpoise, cured 4.5 hr. at 110°C.

^b Basis: 2 nitrogens/molecule.

TABLE VI
Properties of Amine-cured Polymers Reinforced with Added Carbon Black (50 parts)

Curing agent	Sample	<i>i</i> -PBC, mole-%	Viscosity, cpoise	$\frac{[-NH_2]^a}{[-Cl]}$	Tensile strength, psi	Elongation, %
3,3'-Diaminodipropylamine	35B	5.3	56	None	270	240
				0.5	420	410
				1.0	500	220
	32B	1.31	148	None	5	600
				0.2	136	142
				1.2	420	134
				2.0	730	200

^a 3,3'-Diaminodipropylamine, calculated at 2 nitrogens/mole; cure: 20 min. at 160°C.

4½ hr. in 3,3'-diaminodipropylamine at 110°C. The product contained 0.28% N and 0.49% Cl, in agreement with the assumption that two amino groups in the triamine were used in crosslinking.

The incorporation of carbon black and the use of isopropenylbenzyl chloride (*i*-PBC) copolymers of higher viscosity (Table VI) gave somewhat greater improvement in properties. Again it can be seen that there is an optimum amount of curing agent, through it may not have been reached in the series with rubber 32B.

A typical butyl rubber cure gave the most encouraging results. The formula for and results obtained with such a cure are shown in Table VII. A sample of Enjay butyl rubber of type 365 is included for comparison. It is probable that better properties might have been realized with any of these samples if the optimum conditions could have been found.

Morrissey⁸ has described bromine- and chlorine-containing butyl rubber which can be vulcanized

with various conventional rubber cures. Our copolymers ought to have more stability in the unvulcanized state than Morrissey's halogenated aliphatics.

Permselective Membranes

Permselective membranes were prepared by casting films of copolymers containing 50–60 mole-% vinylbenzyl chloride, prepared in the same manner as the copolymers previously described. These films were simultaneously quaternized and crosslinked by immersion in a mixture of dimethylethanolamine and diethylenetriamine for two days. The properties of these films are shown in Table VIII along with those of two commercially available membranes, a Rohm and Haas Amberplex C-1 and an Ionics CR-51. A high specific conductivity is desirable, and a permselectivity of 1.0 is perfect. The conductivity of our films is somewhat higher than those of the commercial films, but the selectivity is lower.

TABLE VII
Standard Butyl Rubber Cure^a

Rubber	Viscosity, cpoise	Carbon black, parts	Cure, time, min.	Tensile strength, psi	Elongation, %
Butyl	265	90	20	780	2120
		25	10	1190	830
		25	20	940	630
IBC-B ^b	44	90	20	123	847
		25	10	807	94
		25	20	540	93
IBC-B ^c	148	50	10	1780	760
		25	10	750	510

^a 50 parts rubber, 5 parts ZnO, and 2 parts stearic acid were compounded at room temperature. After addition of another 50 parts rubber, 1.25 parts sulfur, 1.5 parts tetramethylthiuram disulfide, and 1.0 parts mercaptobenzothiazole, the sample was compounded and molded at 160°C.

^b Sample 30B, 3.79 mole-% *i*PBC (Table IV).

^c Sample 32B, 1.31 mole-% *i*PBC (Table IV).

TABLE VIII
Permselective membranes

Sample	Triamine, wt.-%	Specific conductivity, mho/cm. × 10 ³	Permselectivity
Amberplex	C-1	1	0.98
Ionics	CR-51	7	0.97
A ^a	10	14	0.685
	20	11.3	0.905
B ^a	20	19	0.75

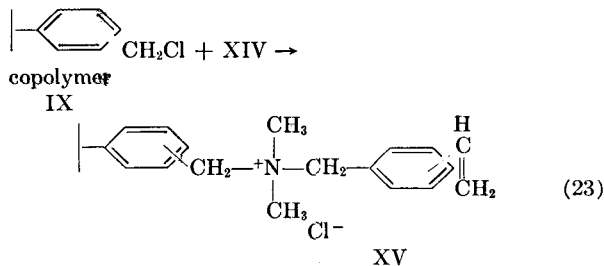
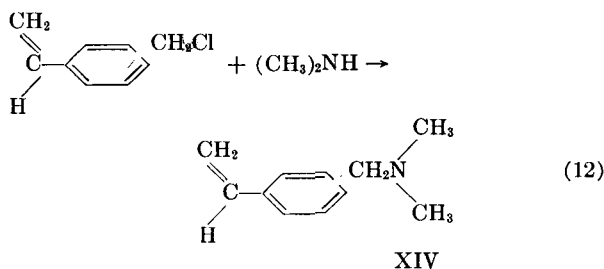
Concentrations: C₁/C₂ = 0.05N/0.1N.

^a Copolymers: (A) 51.5 mole-% VBC; (B) 61 mole-% VBC.

Vinyl-Bearing Polymers for Grafting

An attempt was made to produce a site for grafting by aminating the benzylic chlorine with a vinyl-bearing amine, as shown in eqs. (12) and

(13). The *N,N*-dimethylvinylbenzylamine (XIV) was prepared



from vinylbenzyl chloride and dimethylamine at room temperature; the amination of the copolymer (IX) was then attempted in cumene solution, and the bromine consumption of the product indicated that the reaction had proceeded to at least half the theoretical conversion. The vinyl-containing polymer XV was recovered by precipitation, dissolved in α -methylstyrene, and a grafting copolymerization was attempted, with sodium biphenyl complex as catalyst. The polymers formed showed no improvement in properties over poly- α -methylstyrene. They showed, in fact, the presence of incompatible polymers, suggesting that grafting was incomplete.

The authors wish to acknowledge the work of D. F. Baringer, a summer employee at Dow in 1954, and of W. K. Glesner on this project. The mechanical tests were made by Leo Kin of this laboratory. The nuclear magnetic resonance measurements were made by Dr. J. P. Heeschen of this laboratory.

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Synopsis

The styrene derivatives vinylbenzyl chloride and isopropenylbenzyl chloride were prepared and copolymerized with isobutylene and propylene in order to produce polymers with reactive halogens. Vinylbenzyl chloride and isobutylene have relative reactivities such that the copolymer is much richer in isobutylene than the starting mixture, while with isopropenylbenzyl chloride and isobutylene the difference in reactivities is less and is in the opposite direction. Copolymers containing small amounts of the reactive benzylic chlorine were vulcanized, either with amines or with a conventional butyl rubber cure. Permselective membranes were prepared from copolymers rich in benzylic chlorine.

Résumé

Les dérivés du styrène, le chlorure de vinylbenzyle et le chlorure d'isopropénylbenzyle ont été préparés et copolymérisés avec l'isobutylène et le propylène en vue de fournir des polymères avec des halogènes réactionnels. Le chlorure de vinylbenzyle et l'isobutylène ont des réactivités relatives telles que le copolymère est plus riche en isobutylène que le mélange de départ, tandis qu'avec le chlorure d'isopropénylbenzyle et l'isobutylène, la différence n'est pas si grande et va dans la direction opposée. Les copolymères contenant de petites quantités de chlorure de benzyle réactionnel sont vulcanisés les uns avec des amines, et les autres avec un caoutchouc butylique conventionnel. Des membranes semi-perméables ont été préparées avec des copolymères riches en chlorure de benzyle.

Zusammenfassung

Die Styrolderivate Vinylbenzylchlorid und Isopropenylbenzylchlorid wurden dargestellt und mit Isobutylen und Propylen copolymerisiert, um Polymere mit reaktivem Halogen zu erhalten. Vinylbenzylchlorid und Isobutylen haben derartige relative Reaktivitäten, dass das Copolymere viel reicher an Isobutylen ist als die Ausgangsmischung, während bei Isopropenylbenzylchlorid und Isobutylene der Unterschied nicht so gross ist und in der entgegengesetzten Richtung liegt. Copolymere mit kleinem Gehalt an reaktivem Benzylchlor wurden sowohl mit Aminen, als auch nach einem üblichen Butylkautschukrezept vulkanisiert. Semipermeable Membranen wurden aus Benzylchlorreichen Copolymeren hergestellt.

Received November 29, 1960