

Nucleophilic Displacements upon Poly(vinylbenzyl chloride)

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INTRODUCTION

Forcing displacements upon aromatic chloromethyl groups have been carried out for years in the preparation of anion-exchange resins. With these crosslinked structures varying degrees of hindrance are encountered, especially with resins containing more than 5% divinylbenzene.¹ Recent preparation of the high molecular weight homopolymer of vinylbenzyl chloride^{2,3} has made possible the synthesis of soluble high molecular weight cationic polymers, by reaction of the poly(vinylbenzyl chloride) (PVBC) with *tert*-amines or organic sulfides.^{3,4} This paper examines some of the limitations of reactivity imposed by the polymeric structure itself in linear and in very lightly crosslinked PVBC.

Poly(vinylbenzyl Chloride)

In the present work *ar*-vinylbenzyl chloride prepared by the method of McMaster and Stowe⁵ (66% *para*, 34% *ortho* isomer) was polymerized in emulsion at 30°C., yielding linear polymer of estimated molecular weight about 2×10^6 .³ Lightly crosslinked polymers of microgel structure⁶ were similarly prepared, by adding 0.05% *m*-divinylbenzene to the monovinyl monomer prior to polymerization. In a typical preparation,² deionized water 150 g., 20% aqueous sodium lauryl sulfate (du Pont's Dupanol ME) 15.0 g., 5% aqueous potassium persulfate 6.00 ml., and 5% aqueous sodium bicarbonate 6.00 ml. were combined in a citrate of magnesia bottle and the solution chilled to 3-5°C. To this was added 60.0 g. of a prechilled monomer mixture (vinylbenzyl chloride 99.95% and divinylbenzene 0.050%), and the mixture thoroughly purged with prepurified nitrogen. To the system was then added, with continuing nitrogen purge, 4.10 g. of 5% aqueous sodium metabisulfite, and the bottle capped and placed in a tumbler tank at 30°C. for 16 hr. at 12 rpm. The polymerized latex was then filtered to remove small amounts of coagulum. Conversion to the latex polymer, determined gravimetrically, was 94%. The latex thus prepared contained only traces of monomer.

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General Reactivity

PVBC does not readily undergo many reactions characteristic of non-polymeric benzyl halides. This unreactivity is indicated by the results of several attempts to prepare poly(vinylbenzylamine) from PVBC microgel. A Gabriel reaction was attempted by combining equivalent amounts of dried PVBC and phthalimide with a 10% excess of potassium carbonate. After six hours' refluxing in toluene the solids were collected and hydrolyzed by two cycles of successive reflux in aqueous KOH and aqueous HCl. Elemental analysis showed just 1.5% amination. A Delepine reaction was undertaken by treating another portion of dried PVBC with two equivalents of hexamethylenetetramine and refluxing in chloroform for 4 hr. After decomposition of the resulting complex by warm aqueous HCl the product analysis from this usually clean reaction indicated 27% amination. Other reactions, with aqueous and with anhydrous ammonia in ethanol (seven days at 80°C.), effected greater substitution of amine nitrogens but only at the expense of intermolecular crosslinking. From these several reactions, the distribution of product functional groups as deduced from elemental analysis is shown in Table I. None of the product polymers was soluble in water or in dilute HCl.

The hydrolysis of PVBC microgel was compared with that of *p*-ethylbenzyl chloride. With dilute alkali in 1:1 isopropyl alcohol-water at reflux, *p*-ethylbenzyl chloride underwent a smooth second order hydrolysis, apparent rate constant = 0.63 l. mole⁻¹ min.⁻¹. Under the same conditions PVBC underwent a rapid hydrolysis to the extent of about 7%, but underwent no perceptible further reaction, even upon 24 hr. further refluxing with 1.0M KOH. When the medium was changed to 1:1 dioxane-water, *p*-ethylbenzyl chloride and PVBC both underwent hydrolysis, with apparent rate constants of 2.0 and 0.31 l. mole⁻¹ min.⁻¹, respectively. The emergence of a measurable rate of hydrolysis for PVBC in this latter system suggests the importance of swelling of the latex particles. (Dioxane, unlike isopropyl alcohol, is a solvent for PVBC.) The sharp cutoff of hydrolysis in the alcohol-water systems suggests that the reaction is restricted to surface sites; this corresponds to penetration of about 7 Å. in a 600 Å. latex.

TABLE I
Summary of Attempted Aminations of PVBC Microgel^a

Reaction route	Intact benzyl chloride groups, %	Benzylamine groups, %	Hydrolysis and other reactions, %
Gabriel	89	1.5	9.5
Delepine	73	27	nil
Ammonia, wet	16	40 ^b	44
Ammonia, anhydrous	2	56 ^b	42

^a Based upon elemental analysis kindly provided by P. H. Boyd.

^b Calculated as primary amino groups but actually including dibenzylamine groups.

In contrast to its sluggish behavior in the foregoing reactions, PVBC is readily reactive with a number of other nucleophiles, even under very mild conditions.³ These reactions are explored below.

Displacements with Pyridines

An aqueous reaction mixture containing 0.200*M* PVBC* and 0.400*M* pyridine was transformed upon 24 hr. standing at room temperature from a thin, opaque, milky latex to a very viscous transparent solution of poly-[(1-*ar*-vinylbenzyl)pyridinium chloride], smoothly dilutable and soluble in water in all proportions. This reaction may be accelerated by heating. Thus, a mixture of PVBC 5.00%, pyridine 10.0% (3.85 equivalents), diethylene glycol 73%, and water 12%, upon being placed in a water bath at 80°C., was jelled in 25 min. and was reacted to a brilliantly clear, very viscous solution in 85 min.

TABLE II
Reactions of some Pyridine Bases with PVBC^a

Nucleophile	Reactions at various times ^b				
	18 hr.	46 hr.	97 hr.	164 hr.	214 hr.
3-Picoline	P	C	—	—	—
4-Picoline	P	C	—	—	—
2,4-Lutidine	O	O	C	—	—
2,6-Lutidine	O	O	O	O	O
Picolinic acid	O	O	O	O	O
Nicotinic acid	O	O	O	O	O
Isonicotinic acid	O	O	O	O	O
Nicotinamide	O	O	O	O	O ^c
4-(ω -Hydroxypropyl)pyridine	O	O	P	C	—
4-(ω -Hydroxyethyl)pyridine	O	O	O	—	P
Quinoline	O	O	—	P	C
Isoquinoline	C	—	—	—	—

^a Reactions at room temperature, PVBC 0.200*M*, amine 0.300*M*, medium 30-70 isopropyl alcohol-water.

^b O = no visible reaction; P = partially reacted translucent gel; C = clear and water-soluble (substantially all reacted).

^c Nicotinamide reacts very slowly but eventually to high conversion; see text.

In a series of runs carried out at room temperature (about 26°C.) with PVBC 6.75 g., amine 12.5 ml., isopropyl alcohol 25 ml., and water q.v. 100 ml., pyridine, 3-picoline, 4-picoline, and 2,4-lutidine reacted to form clear, water-soluble polyquaternaries within 63 hr. 2-Picoline had reacted by 200 hr. 2,6-Lutidine, however, remained substantially unreacted after 17 days. The carboxylic acid analogs of the picolines (picolinic, nicotinic, and isonicotinic acids) also failed to react significantly on 17 days' standing. Nicotinamide (3-carbamoylpyridine) yielded a system which was opaque at

* "Molar" concentrations, used for convenience, signify gram-equivalents of vinylbenzyl chloride units per liter.

13 days but nearly transparent after 17 days. From other work in which the kinetics of these displacement reactions have been examined,⁷ this implies reaction of approximately 60% of the chloromethyl sites after 17 days. Quinoline also reacted slowly, yielding a foggy gel at 63 hr. which progressed to a clear, water-soluble polyquinolinium product by 13 days. Isoquinoline reacted more rapidly, giving the clear, water-soluble product in less than 63 hr.

A similar series of runs was carried out with PVBC 0.200M and various amines 0.300M in a 30-70 (by weight) isopropyl alcohol-water mixture. The results, shown in Table II, indicate a similar pattern of reactivity.

Displacements with Aliphatic *tert*-Amines

The fastest reaction encountered in this study is that of PVBC with trimethylamine to form poly[trimethyl(*ar*-vinylbenzyl)-ammonium chloride].³ The next nucleophile of this homologous series, triethylamine, reacts at a much slower rate. Comparative initial rates of reaction with a special sample of PVBC containing 92% *para*-isomer are shown in Figure 1.

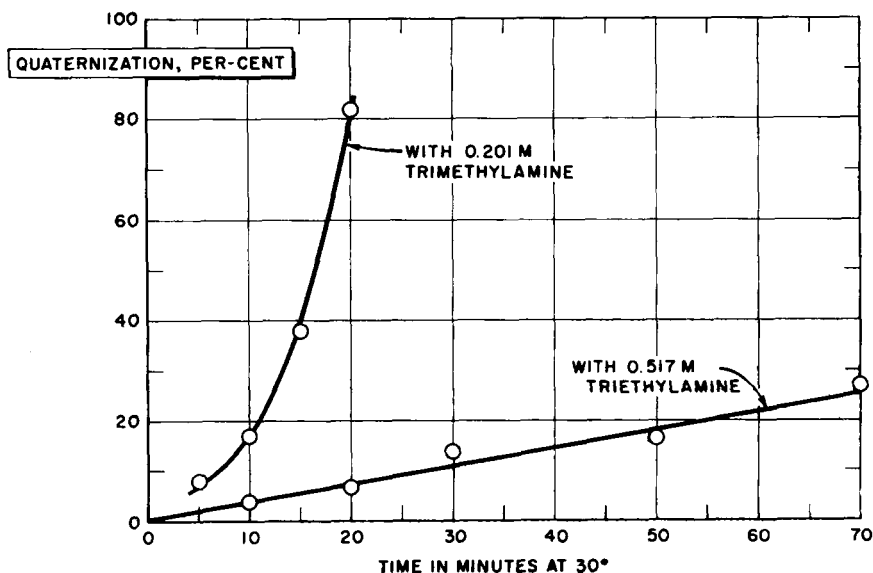


Fig. 1. Quaternization of 0.143M poly(*ar*-vinylbenzyl chloride) 92% *p*-isomer.

With the more hindered⁷ poly(*o*-vinylbenzyl chloride) the reaction rate of triethylamine at room temperature was immeasurably slow. With the mixed isomer PVBC at 0.200M, 0.400M trimethylamine reacted in aqueous medium to give a clear soluble product in well under one day, triethylamine required one month, tri-*n*-propylamine had reacted only slightly at the end of two months, and tri-*n*-butylamine showed no signs of other than surface reaction with PVBC on two months' standing.

Introduction of an organic cosolvent increases the reaction rates. PVBC 6.75 g., triethylamine 12.5 ml. (two equivalents), isopropyl alcohol 25 ml., and water q.v. 100 ml., on mixing vigorously and letting stand at room temperature, yielded a clear viscous syrup of poly[triethyl(*ar*-vinylbenzyl)ammonium chloride] within 63 hr. With PVBC 0.200*M*, triethylamine 0.300*M*, isopropyl alcohol 30 wt.-%, and the balance water, the system jelled in 18 hr. and yielded a clear, water-soluble product polymer in 46 hr. Under similar conditions tri-*n*-propylamine yielded a translucent, partially reacted mixture in 46 hr. and a clear, water-soluble product polymer, poly[tri-*n*-propyl-(*ar*-vinylbenzyl)ammonium chloride], in 150 hr. No method was found, however, to achieve even partial conversions with tri-*n*-butylamine and higher analogs.

On the other hand, *N,N*-dimethyldodecylamine has been found to react in aqueous-methanolic solutions to yield the alcohol-soluble polysoap.³ A series of *N,N*-dimethyl-*n*-alkylamines was prepared by reaction of the corresponding *n*-alkyl bromides with dimethylamine. Portions of aqueous PVBC latex (25% polymer solids) were treated with threefold excesses of the purified *tert*-amines. The first members of this series, from trimethylamine through *N,N*-dimethyl-*n*-hexylamine, reacted within 30 min. at room temperature to yield clear, viscous, water-soluble products. After 2 hr. standing, *N,N*-dimethyl-*n*-octylamine and *N,N*-dimethyl-*n*-decylamine had also reacted to give clear, water-soluble polyquaternaries. Under these conditions higher members failed to react completely, and the branched amine, *N,N*-dimethyl-1-(2-ethyl)hexylamine, failed to react appreciably. Reactions of PVBC 0.0479 moles with 100% excesses of

TABLE III
Solubilities of Reaction Products of PVBC and Dimethyl-*n*-alkylamines

R in reaction product of PVBC and (CH ₃) ₂ NR	Solubilities of resultant polyquaternaries ^a				Toluene-CH ₃ OH mixt. ^b
	Water	CH ₃ OH	Me ₂ CHOH	MeCOEt	
Methyl	S	S	W	W	—
Ethyl	S	S	W	W	—
<i>n</i> -Propyl	S	S	W	W	—
<i>n</i> -Amyl	S	S	S	W	—
<i>n</i> -Hexyl	S	S	S	S	—
<i>n</i> -Octyl	S	S	S	S	—
<i>n</i> -Decyl	S	S	S	S	—
<i>n</i> -Dodecyl	W	S	W	W	S
<i>n</i> -Tetradecyl	W	S	W	W	S
<i>n</i> -Hexadecyl	I	S	W	I	S
<i>n</i> -Octadecyl	I	I	I	I	S
PVBC unreacted	I	I	I	W	—

^a S = soluble; W = swollen or syneresed; I = insoluble.

^b Soluble in methanol-toluene mixtures over the composition range 10-90% by volume methanol.

N,N-dimethyl-*n*-dodecylamine, *N,N*-dimethyl-*n*-hexadecylamine, and *N,N*-dimethyl-*n*-octadecylamine, in a reaction medium of 50 ml. water and 100 ml. methanol, were more successful. On shaking for five days at room temperature these mixtures were transformed into two-phase systems, each consisting of a viscous, buttery top layer containing polymer and excess amine, and a clear fluid lower layer. Solubilities of these polymers are summarized in Table III.

The progressive replacement of methyl groups in trimethylamine with 2-hydroxyethyl groups provides an interesting series with regard to PVBC reactivity. When 10.0 ml. of latex (29% PVBC) was treated with 10 ml. of trimethylamine diluted with water to provide a total volume of 100 ml., the system was converted in a few hours to the clear, water-soluble product polymer. When one methyl group of the amine was replaced (i.e., with *N,N*-dimethylethanolamine), no significant reaction occurred on two months' standing.

In parallel runs in which the 80 ml. of water diluent was replaced with ethylene glycol, the trimethylamine system reacted within 1 hr., the *N,N*-dimethylethanolamine system was reacted to a completely clear, water-soluble product within 60 hr., and the *N*-methyliminodiethanol system was mostly reacted (translucent dispersable gel) within two months.

This last reaction can be forced by heating. PVBC with 100% excess *N*-methyliminodiethanol was diluted with water to yield 10% by weight product polymer solids and the mixture sealed in glass and heated for 24 hr. at 70°C. and 24 hr. at 80°C., whereupon a viscous, clear, water-soluble solution of poly[bis(2-hydroxyethyl)methyl(*ar*-vinylbenzyl)ammonium chloride] was obtained. A combination of heat and polar organic cosolvent is even more efficacious. Mixtures of the three hydroxyethyl *tert*-amines (10% by wt.), PVBC (5%), diethylene glycol (73%) and water (12%) were heated to 82°C. The mixture containing *N,N*-dimethylethanolamine was reacted to clear product polymer within 25 min.; that with *N*-methyliminodiethanol was nearly clear within 90 min. and was fully reacted on standing overnight. Triethanolamine (2,2',2'-nitrolotriethanol) failed to undergo detectable reaction, even upon extended heating in this and other systems.

Displacements with Sulfur Analogs

An aqueous system containing PVBC 0.200*M* and dimethyl sulfide 0.400*M* yielded, on standing about 32 hr. at room temperature, a clear, colorless gel of poly[dimethyl(*ar*-vinylbenzyl)sulfonium chloride], soluble in water in all proportions. Similar reactions with diethyl sulfide and with tetrahydrothiophene yielded opaque white insoluble products after 32 hr.; upon standing an additional 4-6 weeks, however, these were transformed into clear, colorless, water-soluble gels of the corresponding sulfonium polymers. Under similar conditions, no detectable reactions were obtained with 2,2'-thiobis(ethanol), 2,2'-thiodipropionitrile, thiophene, or phenothioxine, on two months' standing. In another experiment, equal volumes of PVBC latex (26% polymer in water) and a 2.00*M* isopropyl

alcohol solution of 2,2'-thiobis(ethanol) were combined and the mixture allowed to stand for four months at room temperature. Only a slight thickening of the opaque latex suspension was observed.

Di-*n*-propyl sulfide, combined under the conditions noted above for diethyl sulfide, appeared to react very slightly on two months' standing; di-*n*-butyl sulfide, diisopropyl sulfide, and di-*tert*-butyl sulfide failed to react perceptibly. 1,4-Oxathiane reacted within two weeks in a 20% isopropyl alcohol medium to yield the nearly clear, water-soluble poly(*ar*-vinylbenzyl-4-oxathianium chloride).

Reasoning from the reactivity pattern observed with trialkylamines, it appeared likely that the larger sulfur nucleophiles with unhindered nucleophile atoms, e.g., sulfides of the structure $\text{CH}_3\text{—S—R}$, might be expected to react satisfactorily. PVBC 0.040 moles and methyl 2-hydroxyethyl sulfide 0.080 moles were combined with 30 g. isopropyl alcohol and water to make 100 ml., and the mixture shaken; within four days it was converted to a clear, viscous solution of poly[methyl-2-hydroxyethyl(*ar*-vinylbenzyl)sulfonium chloride]. A parallel run with ethyl β -methylmercaptopropionate yielded in two and a half days at room temperature a clear transparent gel of poly[methyl(2-carboethoxyethyl)(*ar*-vinylbenzyl)sulfonium chloride]. Similarly, the methyl and ethyl esters of 2-methyl-3-methylmercaptopropionic acid reacted to yield the corresponding sulfonium polymers. All of these sulfonium polymers were soluble in water and in methanol in all proportions.

Displacements with Hindered Amines

Most *sec*-amines and di-*tert*-amines upon reaction with PVBC readily form crosslinked insoluble gels. However, the sharp steric limitations which prevent the reaction with diisopropyl sulfide, 2,6-lutidine, etc., suggested the possibility of using steric control to prepare noncrosslinked polyamines from PVBC. A series of runs was made with 0.025*M* PVBC and 0.125*M* amine in 40–60 isopropyl alcohol–water, the reaction mixtures standing for 85 days at room temperature, with intermittent shaking. None of the reaction products was soluble in the reaction mixtures. However the gelled polymeric reaction products with diisopropylamine, with piperidine, with *tert*-butylamine, and with cyclohexylamine were soluble in 0.10*N* HCl (aqueous) and in 0.05*N* HCl (in 1:1 ethanol–water), indicating clean monoreactions.

Factors Controlling Reactivity

From these patterns of reaction, several generalizations may be tentatively proposed concerning the reactivity of nucleophiles with high molecular weight poly(vinylbenzyl chloride).

(1) Nucleophile strength must be sufficient. The reactivity of tetrahydrothiophene and the nonreactivity of thiophene under identical conditions illustrates this requirement. The failure of the pyridinecarboxylic

acids to react, compared with the reactivities of the corresponding picolines, is probably also due, in part at least, to considerations of nucleophilicity.

(2) Specific steric limitations are imposed, extending well beyond those associated with the corresponding small-molecule reactions. The effects of *o*-methyl substituents on pyridine (cf. 2-picoline vs. 3- and 4-picoline, 2,6-lutidine vs. 2,4-lutidine) indicate the crucial hindrance to be close to the nucleophile atom. This is also supported by the sharp cutoffs in reactivity observed in the homologous tri-*n*-alkylamines and di-*n*-alkyl sulfides. This is further supported by the successful reactions of still larger nucleophiles which have unhindered nucleophile atoms, i.e., those of the types $(\text{CH}_3)_2\text{N}(\text{CH}_2)_n\text{CH}_3$ and $\text{CH}_3\text{SCH}_2\text{CHR}\text{COOR}'$.

(3) The partition coefficient of the nucleophile between the aqueous and polymer phases must permit significant nucleophile concentration in the latter phase. The failure of triethanolamine to react, compared with the reactivities of the sterically similar tri-*n*-propylamine and of various weaker nucleophiles (pyridines and sulfides) appears to be due to its extreme water-compatibility. This may also explain the general deactivating effect of 2-hydroxyethyl groups, as well as the failure of hydroxide ion to penetrate and react with unswollen PVBC.

(4) The reaction medium is of the greatest importance in displacement reactions of this type upon high polymers. A highly polar medium stabilizes the semi-ionic transition state and thereby facilitates the displacement by reducing its activation energy. Furthermore, such a medium tends to solubilize the partially reacted polymer molecules and thereby to facilitate the high conversions which are *not* attainable in systems which precipitate partially reacted polymers. To promote early reactions at low conversions, it is also advantageous to use a polar organic cosolvent, the functions of which may be twofold: (a) to open up the polymer phase by swelling into it, and hence to reduce the steric restrictions upon the nucleophiles (cf. results with tri-*n*-propylamine), and (b) as a vehicle to carry into the polymer phase those nucleophiles which would otherwise remain entirely in the aqueous phase (e.g., methyldiethanolamine, hydroxide ion).

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Synopsis

High molecular weight poly(vinylbenzyl chloride) fails to undergo many classical organic reactions, but may be reacted essentially quantitatively with a variety of *tert*-amines to yield the corresponding quaternary polymers. With dimethyl-*n*-alkylamines, polymers of the type $(C_2H_5-C_6H_4-CH_2NR(CH_3)_2 Cl)_n$ are formed; these are water-soluble through R = *n*-decyl and methanol-soluble through R = *n*-hexadecyl. A number of pyridines and dialkyl sulfides react similarly to yield the corresponding polycationics. These reactions are controlled by several factors not operative in small-molecule reactions: nucleophile partitioning in the initially heterogeneous systems, swelling power of the medium for the reactant polymer, and a sharp steric limitation imposed by the configuration of the high polymer. This steric effect may be exploited by using certain hindered primary and secondary amines to prepare substituted poly-(vinylbenzylamines) which are soluble and noncrosslinked.

Résumé

Le chlorure de polyvinyl-benzyle de haut poids moléculaire n'est pas susceptible de réagir dans plusieurs réactions organiques classiques; il peut cependant réagir quantitativement avec une variété d'amines tertiaires pour obtenir les polymères quaternaires correspondants. On a formé des polymères du type $(C_2H_5-C_6H_4-CH_2-NR(CH_3)_2-Cl)_n$ avec les diméthyl-*n*-alkylamines. Ces polymères sont solubles dans l'eau jusqu'à une valeur de R = décyle et solubles dans le méthanol jusqu'à R = *n*-hexadécyle. Une série de pyridines et de sulfure de dialcoyles réagit de même façon et on obtient les polycations correspondants. Ces réactions sont contrôlées par plusieurs facteurs qui ne peuvent agir dans des réactions avec de petites molécules: la répartition nucléophile dans les systèmes initialement hétérogènes, le pouvoir de gonflement du milieu pour le polymère réactif et une limitation stérique stricte imposée par la configuration du polymère. Cet effet stérique peut être exploité en utilisant des amines primaires et secondaires volumineuses pour préparer des poly-(vinyl-benzylamines) solubles et nonpontées.

Zusammenfassung

Hochmolekulares Polyvinylbenzylchlorid gibt zwar viele klassische organische Reaktionen nicht, es kann aber praktisch quantitativ mit einer Vielfalt von *tert*-Aminen zur Reaktion unter Bildung der entsprechenden quaternären Polymeren gebracht werden. Mit Dimethyl-*n*-alkylaminen werden Polymere vom Typ $(C_2H_5-C_6H_4-CH_2NR(CH_3)_2Cl)_n$ gebildet; diese sind bis zu R = *n*-Decyl wasserlöslich und bis zu R = *n*-Hexadecyl methanollöslich. Eine Anzahl von Pyridinderivaten und Dialkylsulfiden reagieren ähnlich unter Bildung der entsprechenden Polykationen. Für den Ablauf dieser Reaktionen sind mehrere, bei Reaktion kleiner Molekel nicht wirksame Faktoren wichtig: Verteilung des Nucleophilen bei den anfänglich heterogenen Systemen, Quellfähigkeit des Mediums für das reagierende Polymere und eine scharfe, durch die Konfiguration des Hochpolymeren bedingte Begrenzung. Dieser sterische Effekt kann durch Verwendung bestimmter, gehinderter primärer und sekundärer Amine zur Darstellung substituierter, löslicher und unverbundener Polyvinylbenzylamine ausgenutzt werden.

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