

Synthesis and Thermal Stability of Novel Anion Exchange Resins with Spacer Chains

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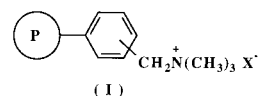
ABSTRACT: Spacer-modified anion exchange resins were prepared by suspension copolymerization of ω -bromoalkylstyrenes or ω -bromoalkyloxymethylstyrenes with 2–8 mol % of divinylbenzene, followed by quaternization with trimethylamine. The thermal stability of the spacer-modified anion exchangers of the OH form was examined by standing the resins in deionized water at 100–140°C for 30–90 days. The anion exchangers with alkylene chains such as butylene or heptylene groups between the benzene ring and the quaternary nitrogen exhibited higher thermal stability compared with commercial, strongly basic anion exchangers with benzylic ammonium groups. The thermal stability of the exchangers with butyleneoxymethylene or hexyleneoxymethylene spacers was also higher than that of the commercial exchangers. The exchanger with the propyleneoxymethylene spacer, however, had less stability than did the commercial ones. The decreased stability of this spacer-modified exchanger is due to the accelerated degradation of the spacer chain via Hofmann elimination. The excellent stability of the anion exchangers with alkylene or alkyleneoxymethylene spacers, except propyleneoxymethylene, results from the structure of the exchangers, where there are no reactive benzylic carbons, which are attached directly to the quaternary nitrogen. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1161–1167, 1997

Key words: anion exchange resin; spacer-modified resin; thermal stability; Hofmann elimination

INTRODUCTION

Styrene-based strongly basic anion exchange resins have been effectively used for a variety of fields such as water treatment, hydrometallurgy, food industry, chemical industry, bioindustry, and so on.^{1–4} However, commercial anion exchange resins such as (I) with benzylic trimethylammonium groups are unstable chemically in the hydroxide form or basic conditions and are not suitable for applications at temperatures above 60°C.^{5–7} The low thermal stability of the exchangers of the

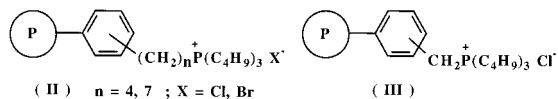
OH form is well known to be due to the increased reactivity (decreased stability) of the benzylic carbon, which is attached directly to the quaternary nitrogen atom.



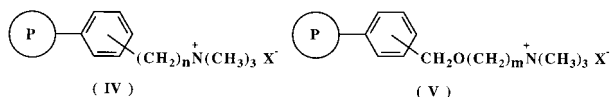
We have already reported that spacer-modified, polymer-supported phosphonium salt catalysts such as (II) have higher chemical stability than do conventional polymer-supported phosphonium salt catalysts such as (III), which contain a benzylic onium structure in reactions of alkyl halides with NaCN under triphase conditions.⁸

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Therefore, the introduction of spacer chains between the benzene ring and the quaternary nitrogen in the anion exchangers is expected to be effective in order to increase the stability of the exchangers. This article reports the synthesis and thermal stability of novel spacer-modified anion exchangers such as (IV) or (V) with alkylene or alkyleneoxymethylene chains, respectively.



EXPERIMENTAL

Materials and Measurements

ω -Bromoalkylstyrenes were prepared by a cross-coupling reaction of vinylbenzylmagnesium chloride with α,ω -dibromoalkanes, according to the method described in the literature.⁸ Other reagents and solvents except ω -bromoalkoxymethylstyrenes were purchased and used without further purification. Infrared (IR) spectra were obtained with a Shimadzu FT-IR 4000 spectrophotometer. ¹H nuclear magnetic resonance (NMR) spectra were recorded on a 270 MHz instrument (JEOL EX-270) with CDCl₃ as the solvent and tetramethylsilane as the internal standard.

Preparation of ω -Bromoalkoxymethylstyrenes

Styrene derivatives with a 4-bromobutoxymethyl or 6-bromohexoxymethyl group were prepared as follows. A 300 mL four-necked flask with a reflux condenser was charged with 40 g of a 50% aqueous NaOH (0.5 mol) and toluene (100 mL) solution containing vinylbenzyl alcohol (a mixture of *m*- and *p*-isomer, 0.1 mol), 1,4-dibromobutane (0.15 mol), and tetrabutylammonium bromide (0.01 mol). The mixture was vigorously stirred at 40°C for 8 h. The separated organic layer was washed with water and dried over anhydrous MgSO₄. After the evaporation of toluene, the residue was distilled under reduced pressure in the presence of 1,1-diphenyl-2-picrylhydrazyl (DPPH): boiling point (bp), 112–117°C/0.6 torr; yield, 56%. IR (neat): 1,630 (C=C); 1,110 (C—O—C); 640

cm⁻¹ (C—Br). NMR (CDCl₃): δ 1.64–1.74 (m, 2H, OCH₂CH₂CH₂CH₂Br); 1.85–1.96 (m, 2H, OCH₂CH₂CH₂CH₂Br); 3.33–3.45 (m, 4H, OCH₂CH₂CH₂CH₂Br); 4.42 (s, 2H, PhCH₂); 5.17–5.23 (m, 1H, *trans* CH₂=); 5.67–5.78 (m, 1H, *cis* CH₂=); 6.61–6.73 (m, 1H, CH=); 7.15–7.36 (m, 4H, phenylene).

3-Bromopropoxymethylstyrene was prepared by another method, because the above method could not afford the monomer with the bromopropoxymethyl group. A 1 L four-necked flask with a condenser was charged with 1,3-propanediol (6.5 mol), NaOH (2.0 mol), and hydroquinone (1.5 g), and the mixture was stirred at 80°C until the sodium hydroxide dissolved. After chloromethylstyrene (a mixture of *m*- and *p*-isomer, 1.6 mol) was added dropwise over 0.5 h to the stirring mixture at 80°C, the mixture was stirred at the same temperature for an additional 0.5 h. After cooling, the reaction mixture was poured into a brine (20%), and the organic layer was separated. The aqueous layer was extracted with toluene, and the extract, combined with the organic layer, was washed with water and dried over anhydrous MgSO₄. After the evaporation of toluene, the residue was distilled *in vacuo* in the presence of DPPH: bp, 101°C/0.42 torr; yield, 60%. IR (neat): 3,400 (OH); 1,630 (C=C), 1,095 cm⁻¹ (C—O—C).

The hydroxypropyl group of this product was converted into the bromopropyl group by treatment with PBr₃. A 300 mL four-necked flask was charged with (3-vinylbenzyloxy)propanol (1.0 mol) and pyridine (55 mL), and PBr₃ (0.4 mol) was added dropwise over 2 h to the stirring mixture at -5–-10°C. After the complete addition, the mixture was stirred for 1 day at room temperature. The mixture was poured into a brine (20%), and the separated organic layer was washed with water and aqueous NaHCO₃ (8%) and dried over anhydrous MgSO₄. After the evaporation of toluene, the residue was distilled *in vacuo* in the presence of DPPH: bp, 100°C/0.52 torr; yield, 35%. IR (neat): 1,630 (C=C); 1,105 (C—O—C); 650 cm⁻¹ (C—Br). NMR (CDCl₃): δ 2.06–2.16 (m, 2H, OCH₂CH₂CH₂Br); 3.48–3.62 (m, 4H, OCH₂CH₂CH₂Br); 4.50 (s, 2H, PhCH₂); 5.020–5.28 (m, 1H, *trans* CH₂=); 5.70–5.79 (m, 1H, *cis* CH₂=); 6.64–6.76 (m, 1H, CH=), 7.18–7.40 (m, 4H, phenylene).

Preparation of Anion Exchange Resins

Suspension polymerization of ω -bromoalkylstyrenes or ω -bromoalkoxymethylstyrenes with divi-

nylbenzene (DVB) was conducted according to the procedure described before.⁹ The typical procedure for the preparation of anion exchangers is as follows. A 1 L three-necked flask with a reflux condenser was charged with 20.0 g of poly(4-bromobutylstyrene) resin crosslinked with 2 mol % of DVB and 200 mL of dioxane. The mixture was stirred for 1 h to swell the resin at room temperature. Then, 200 mL of aqueous trimethylamine (30 wt %) was added dropwise to the mixture at room temperature. The mixture was stirred for an additional 15 h at 50°C. The obtained anion exchanger was separated by filtration; washed thoroughly with deionized water, methanol, tetrahydrofuran, and dichloromethane; and dried *in vacuo* for 15 h at 90°C. The bromide ion content was determined by the Volhard method: 3.21 mEq/g (97% quaternization).

The resin with bromide counter ion was converted to the resin with chloride ion (Cl form) by treatment with aqueous NaCl. The ion exchange capacity of the resin of Cl form was 0.72 mEq/mL.

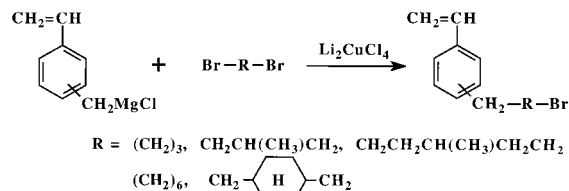
Measurement of Ion Exchange Capacity

The strong base capacity (salt splitting capacity) of anion exchangers was determined as follows. Ten milliliters of anion exchange resin with hydroxide counter ion (OH form) was packed in a column, and 250 mL of 4% aqueous NaCl was passed through the column. The eluent was recovered and titrated with 1N HCl.

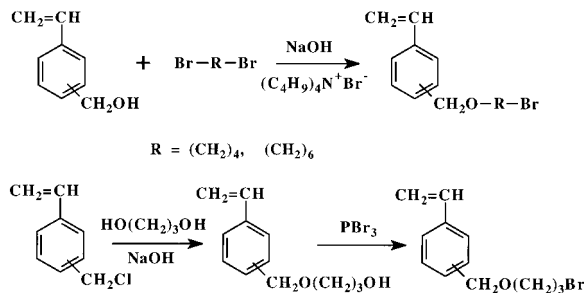
The resin treated with aqueous NaCl was provided for the following determination of weak base capacity. One hundred milliliters of 0.1N HCl was passed through the column containing the anion exchanger of Cl form (10 mL), and 50 mL of methanol was subsequently passed through to rinse the resin. The recovered eluent was titrated with 1N NaOH.

Thermal Stability of Anion Exchangers

A sealed glass autoclave tube was charged with 100 mL of anion exchange resin of the OH form.



Scheme 1



Scheme 2

The resin was held at 100–140°C for 30–90 days in demineralized water. After exposure, the strong and weak base capacities of the resin were measured. The wet resin was dried at 105°C for 4 h, and the moisture content of the resin was determined from the weight decrease. The percentage of residual strong base capacity was calculated as follows: remaining ratio (%) = strong base capacity (per unit volume or weight) of recovered resin after test/strong base capacity (per unit volume or weight) of virgin resin.

RESULTS AND DISCUSSION

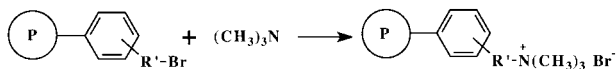
Monomer Synthesis

ω -Bromoalkylstyrenes were prepared in moderate yields (30–48%) by the cross-coupling reaction of vinylbenzylmagnesium chloride with α,ω -dibromoalkanes (see Scheme 1).

ω -Bromoalkoxymethylstyrenes except bromopropoxymethylstyrene were prepared in yields of 50–60% by the phase transfer catalyzed reaction of vinylbenzyl alcohol with α,ω -dibromoalkanes (see Scheme 2). ω -Bromopropoxymethylstyrene, however, could not be synthesized with 1,3-dibromopropane under these conditions: the obtained product was allyloxymethylstyrene. In this case, allyl bromide, produced by the reaction of dibromide with the hydroxide ion, may react with vinylbenzyl alcohol to afford the allyloxymethyl derivative. The desired monomer, therefore, was prepared by reactions via 3-hydroxypropoxymethylstyrene, as shown in Scheme 2.

Preparation of Anion Exchange Resins

The suspension copolymerization of ω -bromoalkylstyrenes or ω -bromoalkoxymethylstyrenes with DVB at 70°C could afford crosslinked poly(ω -bromoalkylstyrene) or poly(ω -bromoalkoxymethyl-



Scheme 3

styrene) in good yields (>90%). The microporous (gel-type) polymer beads were treated with trimethylamine and were converted to anion exchange resins with spacer chains (see Scheme 3). The quaternization of the bromoalkyl group proceeded smoothly to afford gel-type anion exchangers with spacer chains (R') (Table I).

Thermal Stability of Anion Exchangers

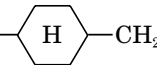
The thermal stability of synthesized and commercial anion exchange resins of the OH form was examined by standing the resins in deionized water at 100–140°C for 30–90 days and was estimated by a comparison of the strong base capacity between the resins recovered after the heat resistance test and the original ones. The results for the alkylene spacer-containing exchangers and the alkyleneoxymethylene spacer-containing ones are shown in Tables II and III, respectively. A commercial DIAION®SA 10A resin (Mitsubishi Chemical) with a benzyltrimethylammonium group exhibited lower thermal stability compared with the alkylene spacer-containing exchangers without benzylic ammonium groups (Table II). The common, commercial anion exchanger with

benzyltrimethylammonium moiety is well known to be decomposed by the nucleophilic substitution of OH⁻ ion on the benzylic or methyl carbon atoms, which results in the decreased strong base capacity (see Scheme 4).^{5–7}

The main reaction in this decomposition is the former one, which liberates the free trimethylamine base. This enhanced reaction on the benzylic carbon must be due to the electron-withdrawing inductive effect and the resonance effect of the benzene ring.

Hatch and Lloyd of Dow Chemical attempted to prepare anion exchangers containing a neophyl ammonium structure without the reactive benzylic ammonium group and examined the thermal stability of the synthesized resin (see Scheme 5).⁶ The resin with the isobutylene group between the benzene ring and the quaternary nitrogen atom, however, did not have the improved stability compared with the common resin with the benzyl group. In this case, the main decomposition proceeded via the nucleophilic attack of the OH⁻ ion on the methyl carbon atom bound to the quaternary nitrogen, whereas the decomposition via the reaction on the methylene carbon adjacent to the nitrogen atom was depressed drastically. The decreased reactivity of the methylene group must be attributed to the steric hindrance caused by the methyl groups in the neophyl quaternary amine structure. The increased reactivity of the methyl group bound to the nitrogen has been considered

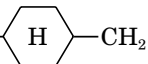
Table I Preparation of Anion Exchange Resins

Spacer Chain ^a (R')	DVB Content (mol %)	Yield of Quaternization (%)	Bromide Ion Content ^b (mEq/g)
(CH ₂) ₄	2	92	3.08
CH ₂ CH ₂ CH(CH ₃)CH ₂	2	92	2.96
	4	83	2.66
(CH ₂) ₃ CH(CH ₃)CH ₂ CH ₂	2	87	2.58
(CH ₂) ₇	2	84	2.49
CH ₂ CH ₂ -  -CH ₂	2	82	2.27
CH ₂ O(CH ₂) ₃	4	85	2.69
	6	88	2.73
	8	90	2.72
CH ₂ O(CH ₂) ₄	4	98	2.90
	6	96	2.81
	8	96	2.75
CH ₂ O(CH ₂) ₆	4	97	2.65

^a See Scheme 3.

^b Determined by the Volhard method.

Table II Thermal Stability of Anion Exchange Resins with Alkylene Spacers

No.	Spacer Chain ^a (R')	DVB Content (mol %)	Strong Base Capacity ^b (mEq/L)		Remaining Ratio ^c (%)
			Initial	After Test ^d	
1	CH ₂ (DIAION® SA10A)		1.42	1.12	79
2	(CH ₂) ₄	2	0.84	0.78 (0.03) ^e	92
3	CH ₂ CH ₂ CH(CH ₃)CH ₂	2	0.77	0.71	92
4		4	1.05	0.91	86
5	(CH ₂) ₃ CH(CH ₃)CH ₂ CH ₂	2	1.01	0.97	96
6	(CH ₂) ₇	2	1.13	1.03	92
7	CH ₂ CH ₂ -  -CH ₂	2	0.93	0.86	93

^a See Scheme 3.^b Values based on Cl form.^c Remaining ratio = strong base capacity of resin after test/strong base capacity of virgin resin.^d Thirty days in OH form at 100°C.^e Weak base capacity after test.

to result from internal steric strain between the methyl groups of the bulky isobutylene group and the methyl groups attached to the quaternary nitrogen.⁶

The anion exchangers synthesized in this study also do not have the reactive benzyl groups, i.e., the ones attached directly to the quaternary nitrogen. The resins, moreover, do not contain any structures with internal steric strains. The increased thermal stability of the alkylene spacer-modified anion exchangers must result from the introduction of less reactive alkylene groups be-

tween the benzene ring and the quaternary nitrogen. However, such structures in the exchangers may lead to decomposition by the Hofmann elimination reaction,¹⁰ as shown in Scheme 6.

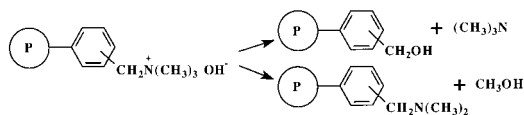
If Hofmann elimination takes place under this heat resistance test, the resins with alkyl groups at the β -position to the quaternary nitrogen atom must be more stable than the resins without alkyl groups at the position.

The resin with the 2-methylbutylene spacer (No. 3 in Table II) exhibited thermal stability comparable to that of the resin with the butylene

Table III Thermal Stability of Anion Exchange Resins with Alkyleneoxymethylene Spacers

No.	Spacer Chain ^a (R')	DVB Content (mol %)	Strong Base Capacity ^b (mEq/g)		Weak Base Capacity ^b (mEq/g)	Remaining Ratio ^c (%)
			Initial	After Test ^d	After Test ^d	
1	CH ₂ (DIAION® SA10A)		3.81	2.77	0.24	73 (57) ^e
2	CH ₂ ^f	2	4.07	2.82	0.20	69
3	CH ₂ O(CH ₂) ₃	4	3.38	0.43	0.20	10
4		6	3.33	0.49	0.22	11
5		8	3.12	0.56	0.23	13
6	CH ₂ O(CH ₂) ₄	4	3.42	3.20	0.13	94 (75) ^e
7		6	3.21	2.87	0.18	89 (74) ^e
8		8	3.32	2.93	0.20	88 (71) ^e
9	CH ₂ O(CH ₂) ₆	4	3.00	2.93	0.09	98

^a See Scheme 3.^b Values based on Cl form.^c Remaining ratio = strong base capacity of resin after test/strong base capacity of virgin resin.^d Thirty days in OH form at 100°C.^e Values after 90 days in OH form at 100°C.^f Derived from crosslinked poly(chloromethylstyrene) prepared by copolymerization of chloromethylstyrene with DVB.

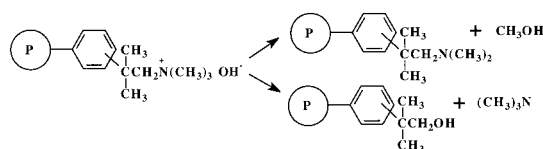


Scheme 4

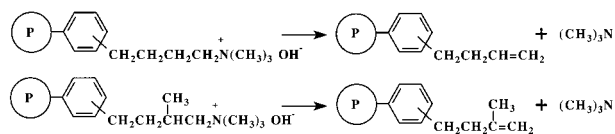
spacer (No. 2 in Table II). The resin with the cyclohexylene structure at the β -position (No. 7 in Table II) also had similar stability compared with the other spacer-modified exchangers. These results suggest that decomposition via Hofmann elimination hardly proceeds in these spacer-modified anion exchangers.

The introduction of alkyleneoxymethylene spacers such as butyleneoxymethylene or hexyleneoxymethylene groups between the benzene ring and the quaternary nitrogen was also effective in increasing the thermal stability of the anion exchangers (Table III). The exchanger with the butyleneoxymethylene spacer exhibited a fairly high remaining ratio even after the test for 90 days (Nos. 6–8 in Table III). However, the exchanger with the propyleneoxymethylene spacer (Nos. 3–5 in Table III) had less stability than the commercial resin DIAION®SA 10A (Mitsubishi Chemical) or a synthesized resin (Nos. 1 and 2 in Table III) with a benzylammonium unit. The IR spectra of the recovered resin containing the propyleneoxymethylene spacer showed absorption bands at 1,640 and 990 cm^{-1} due to $\text{CH}=\text{CH}_2$ linkage (Fig. 1). This result indicates that decomposition takes place via Hofmann elimination, as shown in Scheme 7.

The drastically decreased stability must result from the presence of the propylene group between the quaternary nitrogen and the electronegative oxygen atom, which increase the reactivity (acidity) of the hydrogen atom attached to the β -carbon. Such an electron-withdrawing effect of the oxygen atom decreases with an increasing number of carbon atoms between the oxygen and the β -carbon. The exchangers with alkylene spacers longer than the propylene chain, therefore, are less susceptible to being decomposed by a nucleophilic attack of OH^- .



Scheme 5



Scheme 6

The main decomposition in the anion exchangers containing spacer chains, except the propyleneoxymethylene spacer, as well as in the common ones, was likely to occur at the methylene or methyl carbon adjacent to the quaternary nitrogen. The reactivity of the methylene carbons in the spacer-modified exchangers was reduced largely compared with that of the benzylic methylene carbon in the common exchangers, whereas the reactivity of the methyl carbon of the former did not differ significantly from that of the latter: the reaction of OH^- on the methyl carbon affords the resin with tertiary amine structure (see “weak base capacity” of the recovered resins in Table III).

The thermal stability of the spacer-modified exchangers decreased with an increasing level of crosslinking, although the magnitude of the decrease was not significant (see Nos. 3 and 4 in Table II; Nos. 6–8 in Table III). A similar dependence of the thermal stability of the anion exchanger on crosslinking level has been observed for

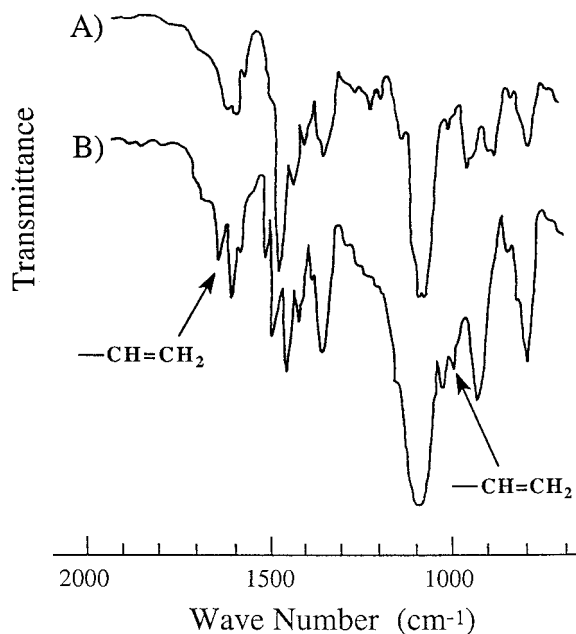
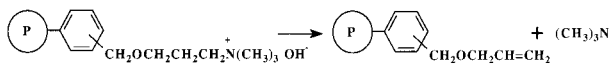


Figure 1 IR spectra of anion exchange resin with propyleneoxymethylene spacer. (A) virgin resin; (B) resin after heat resistance test at 100°C for 30 days.



Scheme 7

a commercial, strongly basic resin, De-Acidite®FF (Permutit Company).⁷ The reduced mobility of the matrix in the exchangers with higher DVB content may result in decreased absorption of the thermal energy, and thereby in the reduced stability of the ammonium groups.⁷

Figure 2 shows the thermal stability of the alkyleneoxymethylene spacer-modified exchangers at 100–140°C. The exchangers with butyleneoxymethylene or hexyleneoxymethylene spacers, crosslinked with 4 mol % of DVB, exhibited excel-

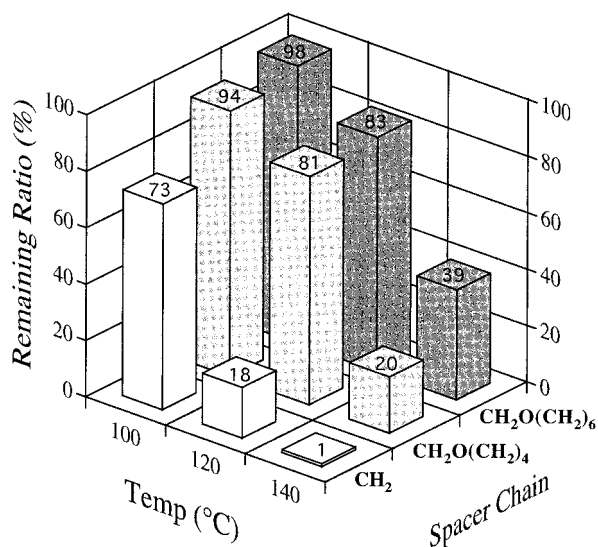


Figure 2 Thermal stability of alkyleneoxymethylene spacer-modified anion exchangers. Heat resistance test conditions: 100–140°C; 30 days.

lent stability at 120°C compared with the commercial exchanger. These spacer-modified exchangers had moderate stability even at 140°C, whereas the commercial exchanger decomposed nearly completely under these conditions.

In conclusion, the introduction of alkylene or alkyleneoxymethylene spacers such as butylene or butyleneoxymethylene chains between the benzene ring and the quaternary nitrogen in strongly basic anion exchange resins was confirmed to improve the thermal stability of the resins. The excellent stability of the spacer-modified anion exchangers results from the fact that the exchangers have no reactive benzylic carbons which are attached directly to the quaternary nitrogen.

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