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FREE RADICAL CROSS-LINKING IN THE PREPARATION OF NON-EXTRACTABLE STATIONARY PHASES FOR CAPILLARY GAS CHROMATOGRAPHY*

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SUMMARY

Free radical cross-linking of methylpolysiloxane stationary phases to form insoluble rubbers recently became of widespread interest in capillary column gas chromatography. The use of various peroxides as free radical generators to form carbon–carbon cross-links in conventional stationary phases has been reported. In this study the applicability of various peroxides and azo compounds for free radical cross-linking and the effects that these free radical generators have on commercially available stationary phases are described. Characteristics of the stationary phases such as chain length and functional groups and their roles in the cross-linking mechanism are discussed. The properties of benzoyl peroxide, dichlorobenzoyl peroxide, dicumyl peroxide, *tert.*-butylperoxide, and azo-*tert.*-butane as free radical generators were evaluated. Stationary-phase polarity change, column activity change and loss of stationary phase were all considered in the overall evaluation of the effectiveness of these free radical generators. Azo-*tert.*-butane showed minimal effect on phase polarity and column activity while benzoyl peroxide and dicumyl peroxide were the most effective in forming insoluble stationary phases.

INTRODUCTION

Although there has been some controversy in the past about the definition of a "bonded phase", the generally accepted characteristic of primary importance is the non-extractability or insolubility of the stationary phase. The advantages resulting from the production of efficient insoluble stationary phases have been described by Grob and Grob[1]. Some of the more important advantages include the ability to wash

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columns of non-volatile compound deposits, minimal phase stripping from injection solvents and enhanced film stability after cross-linking.

Recently, the approach of free radical cross-linking of polysiloxane stationary phases with peroxides to form insoluble rubbers has been reported by several workers[1–5]. This type of cross-linking results in carbon–carbon bonds between methyl groups attached to silicon atoms (Si–C–C–Si). The applicability of this method to several conventional stationary phases as well as some of the aspects of the free radical generator and its use have been examined. In addition to peroxides, certain azo compounds and radiation[6] can also be used as free radical generators. Very little cross-linking (0.1–1 %) is necessary to change long polymeric chains to insoluble rubbers. Consequently, only low levels of cross-linking agent are needed. Adsorption and other undesirable properties resulting from the decomposition of cross-linking agents are minimized since most of the decomposition products are volatile or can be removed from the column with a solvent wash.

The free radical cross-linking of silicone polymers to form insoluble rubbers is well documented and has been performed industrially for many years[7,8]. Unfortunately, this procedure has not been used for the preparation of immobilized stationary phases for capillary chromatography until recently[1]. Free radical cross-linking of stationary phases has been reported earlier, however. One of the earliest examples was reported by Sinclair *et al.*[9] some ten years ago in which the preparation of thermally stable silicone liquid phases by the oxidation of SE-52 on Gas Chrom Q was described. Evans *et al.*[10] have recently examined the deleterious effects of excessive peroxide cross-linking on the efficiency of squalene on Chromosorb G. The approach for capillary columns has previously been the bonding of the phase directly to the column surface, probably due to the influence of high-performance liquid chromatography bonding technology. Grob[11] first attempted this approach using organolithium compounds. Later, Madani *et al.*[12–15] and Blomberg *et al.*[16–20] developed methods in which the condensation of hydroxy and alkoxy groups to split out water, alcohols or ethers were used to form Si–O–Si cross-links in the preparation of non-extractable stationary phases. Problems associated with this approach included the observation of higher activity and lower column efficiencies than were obtained from columns coated with commercial stationary phases. These problems were caused by (a) residual silanol or alkoxy groups left in the phase after cross-linking that cannot be chemically deactivated or thermally removed because of steric problems, and (b) sample molecules being less soluble in the stationary phase as a result of the cross-linking levels (10–50 %, depending on prepolymer chain length) required by this approach. The thermal stabilities of these phases, however, were extremely good owing to the stability of the Si–O–Si bond.

This paper reports the results of an investigation of suitable stationary phases for free radical cross-linking, further studies on the applicability of various free radical producers to this process and the effect of different free radical producers on the final column performance. Various characteristics of the stationary phases such as chain length and functional groups and their roles in the cross-linking mechanism are discussed. The properties of several aroyl and alkyl peroxides and azo compounds as free radical generators are described. The influence of these compounds on column performance was carefully quantified utilizing retention indices to monitor polarity changes, peak asymmetry factors and peak area ratios to assess activity changes and

capacity factor (k') measurements to determine the loss of stationary phase after cross-linking and solvent washing.

EXPERIMENTAL

The following free radical generators were obtained from commercial sources and used as supplied: *tert.*-butyl peroxide (TBP) (Pfaltz and Bauer, Stamford, CT, U.S.A.), azo-*tert.*-butane (ATB) and 2,2'-azobis-(2-methylpropionitrile) (AIBN) (Alfa Products, Danvers, MA, U.S.A.), and dicumyl peroxide (DCP) (Lucidol Pennwalt, Buffalo, NY, U.S.A.). The benzoyl peroxide (BP) (Fischer Scientific, Pittsburgh, PA, U.S.A. or Tridom/Fluka, Hauppauge, NY, U.S.A.) was dried prior to use by dissolving it in benzene followed by separation of the benzene from the water layer and removal of the benzene under reduced pressure. 2,4-Dichlorobenzoyl peroxide (DCBP) was synthesized from 2,4-dichlorobenzoyl chloride (Aldrich, Milwaukee, WI, U.S.A.) following published procedures[21]. Polysiloxane stationary phases were chromatographic grade and were obtained from Applied Science (State College, PA, U.S.A.) or Ohio Valley Specialty Chemicals (Marietta, OH, U.S.A.).

Preliminary testing of various stationary phases with BP, DCBP and AIBN was done by preparing 4% (v/v) solutions in methylene chloride of OV-101, OV-3, OV-17, OV-22, SP-2340, Silar-10C, SE-52, SE-54 and SE-30. These solutions were doped with the desired free radical producer by adding measured volumes of 1% (w/v) solutions of the desired peroxide or azo compound in methylene chloride. These polymer solutions were then put in 0.5-ml Pyrex test tubes and the methylene chloride evaporated under reduced pressure. In all cases the cross-linking was performed by heating the open test tubes in an oven at 150°C. The solubilities of the polymers were then tested by quickly washing with methylene chloride and hexane. If the polymers survived this initial wash they were allowed to sit for 2 h in methylene chloride as a more rigorous test of solubility.

Capillary columns were prepared from uncoated and untreated fused silica capillary tubing (0.20 mm or 0.31 mm I.D.; Hewlett-Packard, Avondale, PA, U.S.A.). Generally, 50-m column lengths were deactivated[22] and then broken into four equal lengths for subsequent coating and cross-linking. Deactivation consisted (in most cases) of first rinsing the column with 5–10 ml of methanol at room temperature. Afterwards, nitrogen was passed through the column for several hours to evaporate any traces of methanol. Next, octamethylcyclotetrasiloxane (D_4) (Ohio Valley Specialty Chemicals) was dynamically coated on the column by filling *ca.* 20% of the column and then rapidly pushing the D_4 plug through the column with nitrogen pressure. After the D_4 plug was expelled from the column, both ends were sealed. Finally, the column was heated for 2 h at 420°C to effect the deactivation. To protect the polyimide outer coating from oxidation during heating, the column was placed in a nitrogen-purged oven or wrapped in aluminum foil and the interior chamber which was formed was purged with nitrogen. After this heat treatment, the column ends were broken and the column was purged with nitrogen for about 30 min at 350°C to remove any residual D_4.

Depending on the type of free radical generator used, the coating and cross-linking procedures differed. For the free radical generators which are solids at room temperature (BP, DCBP, DCP), the peroxide was doped directly into the stationary

phase solution and the column coated normally. However, for the free radical generators which are liquids at room temperature (TBP, ATB), it was necessary to coat the columns first and then saturate the stationary phase with the vapors of the free radical generator. This was done by bubbling nitrogen through the free radical generator and purging the coated columns at 40°C for 2 h.

All columns were statically coated. Fresh coating solutions were prepared daily using purified pentane. The concentration of the stationary phase was selected to give film thicknesses of 0.10 to 0.50 μm. Solutions (0.5–4.0%) of DCP, BP, and DCBP in methylene chloride were also prepared daily and used to spike the coating solutions 30 min prior to coating.

Cross-linking was done by both static and dynamic curing methods. For the static method, the coated columns already containing peroxide were purged with nitrogen and sealed. The columns purged with free radical generator were sealed immediately after disconnecting from the bubbler. The columns were then temperature-programmed from 40°C to the curing temperature at 4°C/min and held for a specified time. The temperature was raised slowly to prevent any stationary phase disruption from the decomposing peroxide. After cross-linking, the columns were washed for 30–60 min with 5–10 ml of methylene chloride. The columns were conditioned with a slow carrier gas flow for 1 h at 40°C to desorb any residual solvent from the stationary phase left from the washing procedure and then temperature programmed to 260°C at 0.5°C/min and held for 8 h. The columns that were coated prior to purging with peroxide or azo compound were conditioned and evaluated prior to and after cross-linking for comparison.

For dynamic curing, columns were attached to an argon manifold in an oven and heated at 5–10°C/min to the curing temperature. Typical conditions for curing were an argon linear velocity of 10 cm/sec and a hold at 250°C for 15–30 min. The columns were rinsed with 10–25 column volumes of methylene chloride–acetone (50:50, v/v) and then conditioned with rapid carrier flow for 30–60 min at ambient temperature. After being reconnected to the argon manifold, the columns were heated at 5°C/min to 350°C and held for 4 h with an argon linear velocity of 25–30 cm/sec.

Columns were evaluated using either a Carlo Erba 4160 gas chromatograph equipped with an on-column injector and a flame-ionization detector (FID) or a Hewlett-Packard 5880A gas chromatograph equipped with a split injector and a FID. Two test mixtures, one containing acidic components and the other containing basic components, were used. Hydrogen carrier gas was adjusted to a linear velocity of 30–45 cm/sec for each column. The oven was temperature-programmed from 40°C after a 2-min isothermal period at 4°C/min to *ca.* 160°C. The sensitivity was adjusted to give full-scale peak height for approximately 1 ng of dodecane. The FID signal from the Carlo Erba gas chromatograph was also connected to the external analog imput of a HP 5880A gas chromatograph and the data processed to give accurate retention times and cardinal point data for peak asymmetry calculations.

RESULTS AND DISCUSSION

Of the polysiloxane stationary phases tested in the 0.5-ml test tubes, only SE-30, SE-52 and SE-54 gave insoluble coatings with 2% or less of the free radical generators. Satisfactory insoluble films were formed with benzoyl peroxide loadings

of 0.2%, 0.5% and 1.0% (w/w), respectively, in SE-30, SE-54 and SE-52. Loadings of 0.2% and 0.5% benzoyl peroxide in SE-54 and SE-52, respectively, washed out slightly with the methylene chloride rinses, but were almost entirely dissolved on sitting in methylene chloride for more than 1 h. SE-54 and SE-30 each required at least 2% AIBN to give insoluble polymers and OV-101 was still soluble with an 8% loading. Furthermore, the use of AIBN resulted in the discoloration of the polymer. These unsatisfactory results for AIBN discouraged any further testing with this azo compound.

Two other stationary phases were also rendered insoluble with peroxides. OV-101 required at least 4% (w/w) benzoyl peroxide and OV-3 required 10% (w/w) benzoyl peroxide to form insoluble rubbers. No other polysiloxane materials tested resulted in non-extractable materials. Higher than 10% (w/w) loadings of peroxides were not tried. The amount of 2,4-dichlorobenzoyl peroxide required was found to be roughly 1.5 times that of the benzoyl peroxide in all cases. This is reasonable since the molecular weight of the dichloroperoxide is about 1.5 times that of benzoyl peroxide.

The influence of the initial polymer chain length on the level of peroxide or azo compound needed is clearly shown in a comparison of the percentages required to yield sufficiently insoluble rubbers from SE-30 and OV-101. OV-101 has a polymer chain length that is *ca.* 0.04 times that of SE-30, and it required roughly 25 times as much peroxide to make it insoluble. SE-30 consists of extremely long chains and therefore requires very few cross-links to render it insoluble. Clearly, long-chain polymeric materials are to be preferred when low levels of peroxide additives are sought.

The functional groups present in the siloxane polymer also have a definite effect on the polymerization reactions and on the nature of the cross-linked product obtained. An understanding of the chemical processes leading to cross-links between polysiloxane chains helps to explain this. Cross-linking of polysiloxanes with free radicals occurs in mechanisms[23,24] similar to that shown in Fig. 1. In the case of polysiloxanes containing vinyl groups the principle cross-linking reaction is not methyl-to-methyl cross-linking as shown, but rather methyl-to-vinyl cross-linking[25,26]. The increased tendency of vinyl groups to cross-link over other functional groups is advantageous since lower levels of peroxides are necessary to achieve similar or higher levels of cross-linking[27]. This can be illustrated by a comparison between SE-52 and SE-54. Both polysiloxanes contain 5% phenyl, but the SE-54 also contains 1% vinyl. The SE-54 required 2.5 times less benzoyl peroxide than the SE-52 to achieve the same level of insolubility. Another example of the tendency for vinyl groups to cross-link is the spontaneous cross-linking of SE-54 when conditioned at 400°C for a

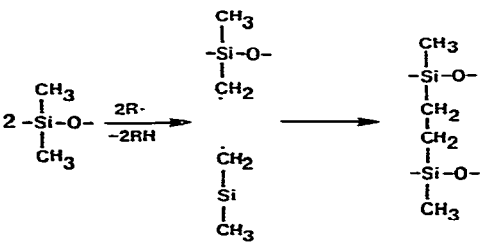

Fig. 1. Typical free radical cross-linking mechanism of polysiloxanes.

few hours. When an SE-54 column was conditioned in this way, only 50% of the phase was extractable, whereas an OV-1 column similarly treated was totally extractable.

In the absence of vinyl groups the cross-linking efficiency of the more reactive aroyl peroxides is low with only 10–30% of the peroxide molecules giving rise to ethylene bridges between siloxane chains[25,28]. Less reactive free radicals formed from alkyl peroxides and azo compounds tend to be vinyl specific, forming free radicals primarily from vinyl groups. The vinyl-specific free radicals will cross-link polysiloxanes containing no vinyl groups, but higher levels of the azo or peroxide free radical producer are required[28]. The higher reactivity of peroxides in the presence of vinyl groups can be attributed to more than one cross-link being formed per molecule of decomposing peroxide[28,29].

Results from experiments using vinyl-specific peroxides[3] showed that 36% of SE-52 (no vinyl) stationary phase was extractable after cross-linking with the vinyl-specific dicumyl peroxide, whereas only 14% of the stationary phase in a similarly cross-linked SE-54 (vinyl-containing) column was extractable. This same point was illustrated by the *tert.*-butyl peroxide cross-linking of a SE-52 column. By measuring k' before cross-linking, and again after cross-linking and solvent washing it was determined that 23% was extracted, compared to less than 5% when SE-54 was similarly cross-linked.

Phenyl groups in the polysiloxane framework markedly hinder free radical cross-linking[8]. This is exemplified by a comparison between the peroxide levels required for SE-30 and SE-52. Both of these polysiloxanes are similar in chain length, but SE-52 with 5% phenyl groups on the siloxane chain required between three and five times more peroxide than SE-30 to give an insoluble polymer. As the phenyl content increases, cross-linking becomes more difficult simply because the phenyl groups are non-reactive. OV-3 (10% phenyl) required 10% benzoyl peroxide to render it insoluble. Grob and Grob[1] have reported the upper phenyl limit for feasible cross-linking to be 33% (OV-61). This conclusion was based on experiments using commercially available phenyl siloxanes which are composed of relatively short-chain polymers. Recent work in this laboratory[30] has shown that methylphenylpolysiloxane gum phases containing greater polymer chain lengths and containing up to 70% phenyl groups can be easily cross-linked, although peroxide levels greater than required for methylpolysiloxanes are necessary.

Typical data illustrating the stability of variously prepared cross-linked columns as assessed by the change in k' before and after solvent washing are given in Table I. It appears that after a minimum threshold amount of peroxide was reached, additional peroxide did not significantly decrease the amount of phase that was extractable. Generally, additional solvent washes did not significantly remove any additional stationary phase.

The effects of vinyl substitution, phenyl substitution, chain length and peroxide specificity were investigated simultaneously with OV-1 and SE-54 cross-linked with BP or DCP. When SE-54 and OV-1 were cross-linked with BP, similar amounts were extracted. Cross-linking with DCP gave 5% extraction for SE-54 and 15% extraction for OV-1. Although the absolute amounts extracted were different, the ratio of amount extracted between OV-1 and SE-54 did not change as the BP was varied between 0.1 and 2.0% and the DCP between 0.5 and 3.0%. The vinyl groups in the

TABLE I

LOSS OF STATIONARY PHASE AFTER CROSS-LINKING AND SOLVENT RINSING

Stationary phase	*Column I.D. (μm)*	*Film-thickness (μm)*	*Crosslinking agent*	*Cure conditions**		*Loss of stationary phase (%)*
				Temperature (°C)	*Time (min)*	
OV-1	310	0.5	0.1% BP	Dynamic		8
OV-1	310	0.5	0.05% BP	Dynamic		22
SE-54	310	0.5	0.1% BP	Dynamic		6
SE-54	310	0.5	0.05% BP	Dynamic		8
SE-54	200	0.1	2% BP	Dynamic		4
SE-54	200	0.1	2% DCP	Dynamic		6
SE-54	310	0.25	0.25% BP	150	120	<1
SE-54	310	0.25	0.25% BP	135	15	6
SE-54	310	0.25	ATB	220	15	15
SE-54	310	0.25	TBP	165	120	5
SE-54	310	0.25	TBP	220	15	5
SE-54	310	0.25	0.28% DCP	175	15	<1
SE-54	310	0.25	0.38% DCBP	115	15	39
SE-54	310	0.25	0.38% DCBP	120	30	33
SE-54	310	0.25	0.38% DCBP	150	120	13

* Static cross-linking unless specified differently.

SE-54 easily compensated for the 5% phenyl content and an initial chain length of about one-half that of OV-1. The vinyl preference of DCP is again quite clear.

Various free radical generators react with and modify to different degrees the polysiloxane being cross-linked. This is largely accounted for by the reactivity of the free radicals and by the nature of the decomposition products which are formed. Ideally, low decomposition temperatures and non-polar and unreactive decomposition products are desired. It is possible that the decomposition products can be incorporated into the polysiloxane chain. Therefore, any polar products would tend to make the phase active and also alter its polarity. Higher decomposition temperatures enhance this possibility. High cross-linking temperatures can also be a serious problem for the more volatile free radical generators if dynamically cured (loss of generator by evaporation). However, this problem can be completely eliminated by static curing (ends sealed).

Data which indicate the reactivity of the free radical generators used in this study are contained in Table II. The decomposition temperature which is listed is the temperature at which 50% of the cross-linking agent decomposes in 15 min. The aroyl peroxides tend to be the most reactive, thus allowing cross-linking to be done at the lowest temperatures. However, they also form the most polar decomposition products. The major decomposition products of DCBP are *m*-dichlorobenzene and 2,4-dichlorobenzoic acid, and those of BP are benzene and benzoic acid. Although, a portion of these products can be removed by solvent washing or mild conditioning, residual amounts of these acids can cause degradation of the polysiloxane framework with exposure at elevated temperatures[27,31]. Such decomposition reactions produce silanol and silicon ester groups, both of which are capable of adsorptive interactions with acids, alcohols and amines. The major decomposition products of the alkyl

TABLE II

REACTIVITY DATA OF VARIOUS FREE RADICAL GENERATORS

Free radical generator	*Activation energy (kcal/mole)*	*Decomposition temperature* (°C)*	*Ref.*
Bis-2,4-dichlorobenzoyl peroxide	28.1	87	35
Dibenzoyl peroxide	29.9	109	36
Di-*tert.*-butyl peroxide	37.5	160	36
Dicumyl peroxide	38.0	142	36
2',2'-Azobutane	43.0	187	37

* Temperature for $t_{1/2} = 15$ min.

peroxides are less polar. The by-products of TBP are acetone and methane and those for DCP are acetophenone and 2-hydroxy-2-phenylpropane[25,27]. These products are not extremely polar or acidic and would not be expected to cause polysiloxane degradation under normal conditions. These peroxides decompose at higher temperatures than the aroyl peroxides, however. The major decomposition products of ATB are nitrogen, isobutane and isobutene. These products are completely non-polar and very unreactive with the polysiloxane chain. No acidic compounds are formed which could react to cause activity problems. ATB is, unfortunately, the least reactive of the free radical producers and requires high temperatures to obtain acceptable free radical generation rates.

Another disadvantage associated with the aroyl peroxides is their low solubility in the methylpolysiloxane stationary phases. In the preliminary test-tube tests in which the methylene chloride was evaporated, crystals of the doped peroxide could be detected at 0.5% levels in the polymer and were abundant in 1.0% and higher levels. After cross-linking, irregularities in the polymer coating on the insides of the test tubes could be seen where crystals previously existed. This was particularly evident for BP. Another indication of problems associated with the aroyl peroxides was the presence of a light brown discoloration of the polymer[27]. With BP this discoloration could be observed at all levels tested, but with DCBP this was only observed at levels greater than 8%. Part of this discoloration was removed with the methylene chloride washes, but even on prolonged exposure (overnight), the intensity was only reduced by about half of the original. This residue is likely a source of undesireable activity. The poor solubility of BP in the non-polar polysiloxanes probably leads to its reacting with itself and, thereby accounting for the discoloration problem.

In addition to the slight increases in acidity resulting from the decomposition products of the free radical generators, the surface of fused silica itself is slightly acidic. This has been experimentally deduced from the tailing peak shapes of the basic alkyl amines and the reduced peak height of the methylated aniline using the classic acid–base test mixture on columns prepared with undeactivated fused silica. Consequently, it was necessary to develop a deactivation procedure that gave an essentially inert surface before the effects of various free radical generators and curing conditions could be properly assessed. Part of the residual acidic surface activity of fused silica is due to deposits of nitrates and nitrites formed during the high-tempera-

ture drawing process from the pyrolysis of atmospheric oxygen and nitrogen[32]. Removal of these deposits with a mild water rinse followed by D_4 deactivation to block the silanol groups gave significant improvement to column inertness, but was still incomplete[33]. Rinsing with methanol instead of water, however, gave better results. Not only were the inorganic ions removed, but the surface was not hydroxylated to the same extent as with water rinsing, and the surface-adsorbed methanol probably catalyzed the D_4 reaction.

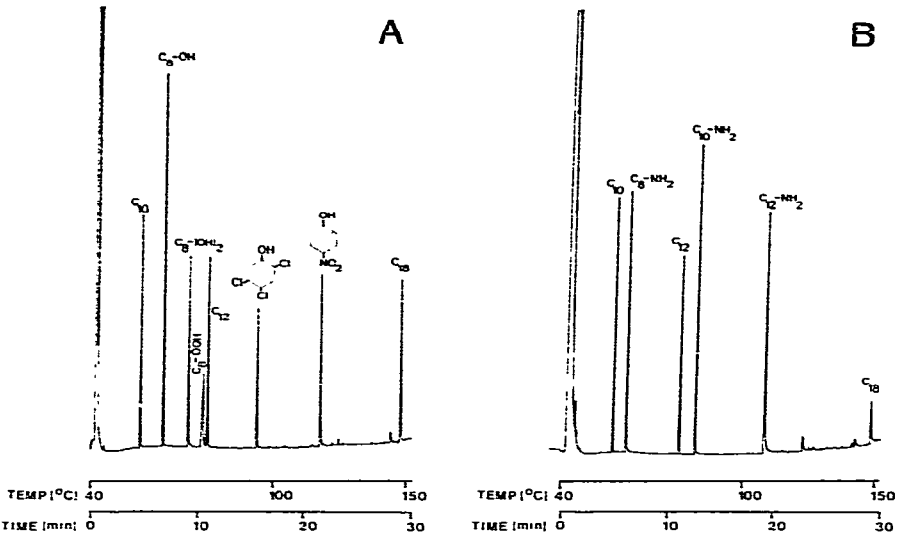

Fig. 2. Capillary gas chromatograms of (A) an acidic test mixture and (B) a basic test mixture obtained on a methanol-washed and D_4-deactivated fused-silica column (11 m × 0.31 mm I.D.) coated with an uncross-linked 0.25-μm film-thickness of SE-54. Chromatographic conditions: temperature programmed at 4°C/min from 40°C after a 2-min isothermal period after injection. Hydrogen carrier gas at 45 cm/sec linear velocity. Sensitivity set for full-scale response for 1 ng of dodecane.

Chromatograms of an acidic and a basic test mixture obtained on a methanol-rinsed and D_4-deactivated fused-silica column coated with SE-54 are shown in Fig. 2. The components in the acidic test mixture (chromatogram 2A) including a highly acidic free fatty acid and a very polar diol all have very symmetrical peaks, and the nitrophenol and C_8-diol have essentially the same peak heights as the dodecane reference, all three of which were in essentially the same stoichiometric concentration (see Tables IV and V for a quantitative description of the column inertness). Likewise, the components in the basic test mixture (chromatogram 2B) have very symmetric peaks shapes and the peak heights of the basic amines compared to the dodecane reference coincide with their stoichiometric concentrations. These results indicate that the finished column had a very inert surface with little residual acidic surface activity.

Several SE-54 columns were cross-linked with the various free radical generators and carefully evaluated to compare their effectiveness. Care was taken to ensure that all the column parameters (except for the different cross-linking procedures) and

operating conditions were standardized. The concentrations of the free radical generators were chosen to be slightly above the minimum threshold values to maximize phase stability and to minimize the deleterious effects of the decomposition products. The concentrations of the solid peroxides were adjusted to give equivalent mole percentages (*e.g.* BP = 0.25; DCBP = 0.38; DCP = 0.28%). The vapors of ATB and TBP were purged through the columns for a sufficiently long time to ensure maximum saturation of the SE-54 stationary phase. It appears that this method provided an evenly treated surface and a homogeneously cured insoluble rubber. Typical chromatograms obtained on columns cross-linked with the five different free radical generators of the same acidic and basic test mixtures as shown in Fig. 2 are shown in Figs. 3–7.

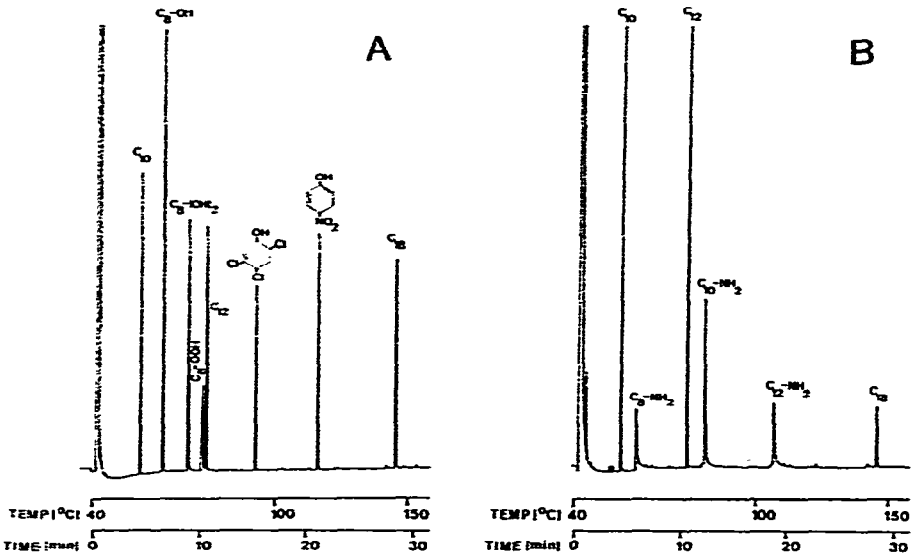

Fig. 3. Capillary gas chromatograms of (A) an acidic text mixture and (B) a basic test mixture obtained on a methanol-washed and D_4-deactivated fused-silica column (11 m × 0.31 mm I.D.) coated with a 0.25-μm film-thickness of SE-54, cross-linked with 0.25% (w/w) BP, and cured at 135°C for 15 min followed by a methylene chloride wash. Chromatographic conditions as in Fig. 2.

The cross-linking efficiency of the five free radical generators and the effectiveness of different static-curing conditions were evaluated by measuring the loss of stationary phase after rinsing with methylene chloride (See Table I). For those columns treated with TBP and ATB, k' measurements for C_{10}, C_{11} and C_{12} at 60°C were made before and after cross-linking and solvent washing. For columns which were cross-linked and washed prior to evaluation, predicted k' values obtained from the average of several identical uncross-linked and non-extracted columns were used to obtain these data. It is clear that some free radical generators are more efficient than others, and that the proper curing conditions are necessary. From the decomposition properties of the free radical generator, reasonable curing conditions were calculated. To prevent any thermal rearrangements and possible adverse activity increases, the most mild curing conditions possible were preferred. However, under-

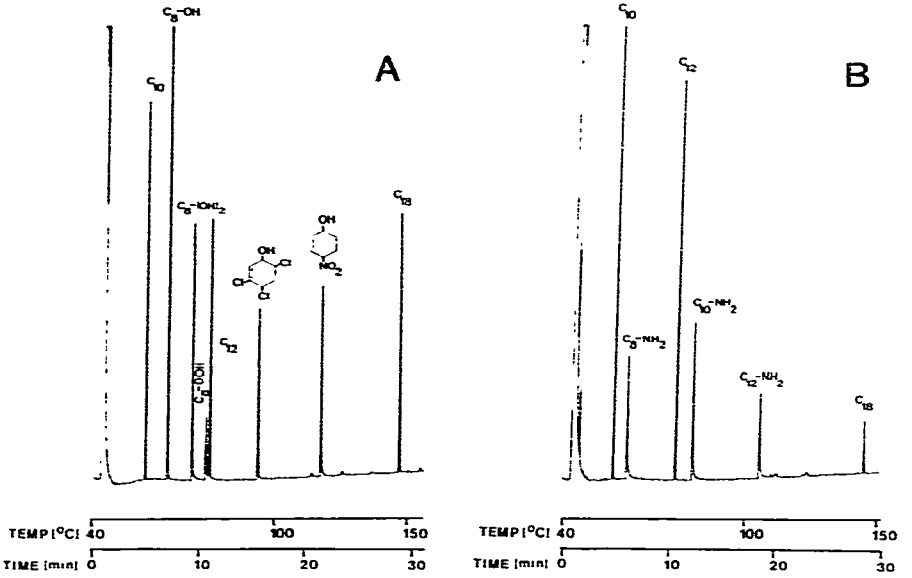

Fig. 4. Capillary gas chromatograms of (A) an acidic test mixture and (B) a basic test mixture obtained on a methanol-washed and D_4-deactivated fused-silica column (11 m × 0.31 mm I.D.) coated with a 0.25-μm film-thickness of SE-54, cross-linked with 0.38% (w/w) DCBP, and cured at 150°C for 2 h followed by a methylene chloride wash. Chromatographic conditions as in Fig. 2.

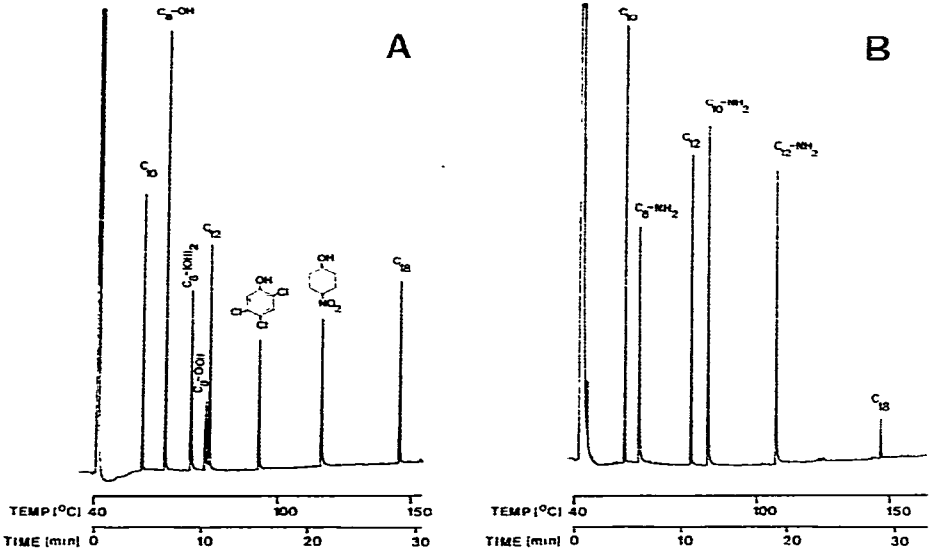

Fig. 5. Capillary gas chromatograms of (A) an acidic test mixture and (B) a basic test mixture obtained on a methanol-washed and D_4-deactivated fused-silica column (11 m × 0.31 mm I.D.) coated with a 0.25-μm film-thickness of SE-54, cross-linked with 0.28% (w/w) DCP, and cured at 175°C for 15 min followed by a methylene chloride wash. Chromatographic conditions as in Fig. 2.

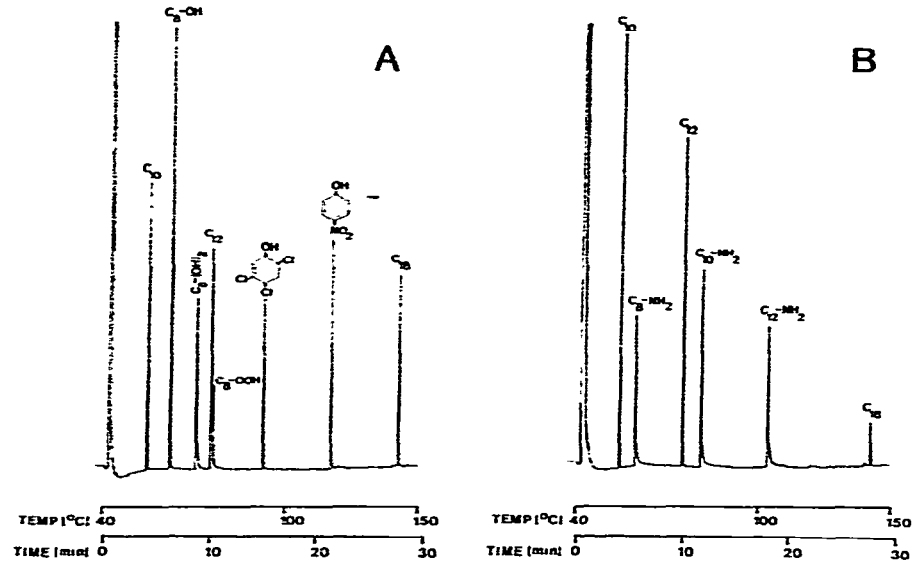

Fig. 6. Capillary gas chromatograms of (A) an acidic test mixture and (B) a basic test mixture obtained on a methanol-washed and D_4-deactivated fused-silica column (11 m × 0.31 mm I.D.) coated with a 0.25-μm film-thickness of SE-54 cross-linked with TBP, and cured at 220°C for 15 min followed by a methylene chloride wash. Chromatographic conditions as in Fig. 2.

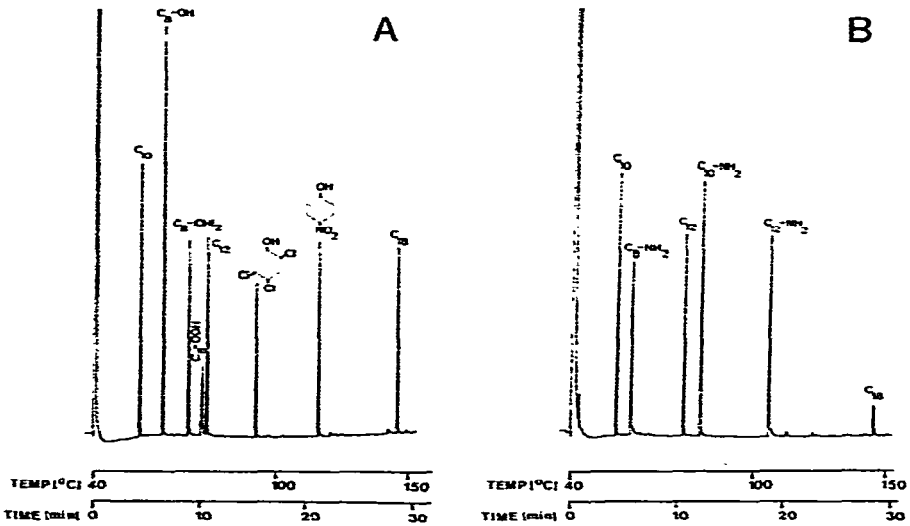

Fig. 7. Capillary gas chromatograms of (A) an acidic test mixture and (B) a basic test mixture obtained on a methanol-washed and D_4-deactivated fused-silica column (11 m × 0.31 mm I.D.) coated with a 0.25-μm film-thickness of SE-54, cross-linked with ATB, and cured at 220°C for 15 min followed by a methylene chloride wash. Chromatographic conditions as in Fig. 2.

curing led to the loss of significant stationary phase which is also undesireable (*e.g.* DCBP, 115°C, 15 min).

To assess any changes in polarity of the cross-linked SE-54 induced by the incorporation of decomposition products into the phase, careful retention measurements were made on each cross-linked column and compared to retention measurements on uncross-linked SE-54. A retention system was defined in which all of the acidic or basic test components were bracketed between decane and octadecane. The relative position of the test compounds between these standards could then be determined. Consequently, it was possible to calculate retention changes between cross-linked and uncross-linked SE-54, and thus, detect subtle changes in phase polarity. These retention change data are tabulated in Table III. Several identical columns and several chromatographic runs on the same column were used to obtain these data. A positive shift in retention indicates that the components were being eluted earlier which suggests that the phase was becoming less polar. On the other hand, a negative retention shift indicates that the components were being retained longer which suggests that the phase was becoming more polar. This is exemplified by a comparison of ATB and BP. The decomposition products of ATB are non-polar, and if incorporated into the phase, would be expected to make it less polar. The decomposition products of BP are polar and should increase the polarity of the SE-54. These examples are verified by the data in Table III. The greatest polarity changes were surprisingly observed when TBP was used as the cross-linking agent. The alkoxy-type decomposition products were evidently incorporated into the SE-54 phase to a significant extent. The free fatty acid actually elutes after the dodecane (see Fig. 6A) rather than before it as usual. The more harsh curing conditions for TBP (220°C, 30 min *vs.* 165°C, 120 min) also tended to increase the polarity of the cross-linked phase.

Probably the most serious problem encountered in free radical cross-linking has been the increased column activity from the free-radical-generator decomposition products. The inertness of the finished columns was evaluated in two ways. Both reversible and irreversible adsorption mechanisms were monitored. Reversible adsorption characterized by peak tailing was quantified with peak asymmetry factors[34]. Using this system, a perfectly symmetrical peak has an asymmetry factor of 1.00. Peaks tailing on the trailing edge (adsorption) have asymmetry factors greater than 1.00, and peaks with the leading edge tailing (overloaded) have asymmetry factors less than 1.00. Peak asymmetry factors for the acidic and basic test components calculated from the chromatographic runs in which the chromatograms shown in Figs. 2–7 were obtained are given in Table IV. Except for the alkyl amines, the peaks exhibited excellent symmetry. The BP caused the greatest increase in peak asymmetry while the DCBP, TBP, DCP and ATB had minimal influences. In most cases, the shapes of the alcohol, diol and acidic phenol peaks were nearly as sharp as the alkane peaks.

In addition to reversible adsorption, irreversible adsorption is an important factor in column inertness. Compounds undergoing this type of adsorption are characterized by symmetric peak shapes, but reduced chromatographic peak areas or heights. This phenomenon was evaluated by comparing the ratio of the peak areas of the test compounds to the area of the dodecane peak contained in the test mixture. The matching peak area ratio data for the chromatographic runs listed in Table IV and shown in Figs. 2–7 are given in Table V. Once again, the most significant effects

TABLE III

RETENTION CHANGES* FOR VARIOUSLY CROSS-LINKED SE-54 COLUMNS

Test compound	*Retention number***	*Cross-linking procedures*						
		BP (0.25%) 135°C, 15 min	*BP (0.25%) 150°C, 120 min*	*DCBP (0.38%) 150°C, 120 min*	*DCP (0.28%) 175°C, 15 min*	*TBP 165°C, 120 min*	*TBP 220°C, 20 min*	*ATB 220°C, 15 min*
C_8-OH	11.33 ± 0.11	−0.08 ± 0.06	−0.17 ± 0.08	−0.24 ± 0.14	−0.17 ± 0.09	−0.04 ± 0.12	−0.49 ± 0.17	+0.21 ± 0.04
C_8-diol	5.37 ± 0.02	−0.05 ± 0.02	−0.08 ± 0.01	−0.08 ± 0.03	−0.07 ± 0.03	−0.23 ± 0.03	−0.26 ± 0.04	+0.06 ± 0.02
C_8-FFA	4.09 ± 0.00	−0.03 ± 0.01	−0.05 ± 0.01	−0.02 ± 0.03	−0.10 ± 0.03	−0.26 ± 0.04	−0.30 ± 0.03	+0.04 ± 0.04
C_{12}	3.86 ± 0.03	+0.01 ± 0.02	−0.01 ± 0.02	+0.06 ± 0.04	−0.01 ± 0.02	+0.07 ± 0.03	+0.10 ± 0.02	+0.06 ± 0.01
Trichloro-phenol	2.23 ± 0.01	0.00	0.00	+0.02 ± 0.01	−0.01 ± 0.01	−0.07 ± 0.01	−0.07 ± 0.01	+0.02 ± 0.01
Nitro-phenol	1.45 ± 0.00	−0.01 ± 0.00	−0.01 ± 0.00	0.00	−0.01 ± 0.00	−0.08 ± 0.00	−0.09 ± 0.00	0.00
C_8-NH_2	19.65 ± 0.79	−1.60 ± 0.76	−5.49 ± 1.04	−0.90 ± 0.59	−1.65 ± 0.43	−3.63 ± 0.16	−2.69 ± 0.37	−0.38 ± 0.20
C_{12}	3.87 ± 0.04	+0.01 ± 0.02	−0.01 ± 0.02	+0.08 ± 0.05	−0.02 ± 0.03	+0.08 ± 0.02	+0.12 ± 0.02	+0.06 ± 0.01
C_{10}-NH_2	3.11 ± 0.03	−0.02 ± 0.03	−0.11 ± 0.03	−0.03 ± 0.03	−0.03 ± 0.02	−0.04 ± 0.02	−0.02 ± 0.01	−0.01 ± 0.01
C_{12}-NH_2	1.70 ± 0.01	−0.01 ± 0.01	−0.02 ± 0.01	0.00	−0.01 ± 0.01	−0.01 ± 0.00	0.00	0.00

* "+" Change indicates earlier elution and "−" change indicates retarded elution.

** Retention number $= \dfrac{R_{C_{18}} - R_{C_{10}}}{R_{\text{Test compound}} - R_{C_{10}}}$, where R is the retention time.

TABLE IV

PEAK ASYMMETRY FACTORS* (A_s) FOR VARIOUSLY CROSS-LINKED SE-54 COLUMNS

Test compound	*Cross-linking procedures*						
	Uncross-linked	*BP (0.25%) 135°C, 15 min*	*DCBP (0.38%) 150°C, 120 min*	*DCP (0.28%) 175°C, 15 min*	*TBP 165°C, 120 min*	*TBP 220°C, 20 min*	*ATB 220°C, 15 min*
C_{10}	1.19	1.20	1.03	1.08	1.13	1.16	1.08
C_8-OH	1.25	1.74	1.32	1.42	1.09	1.14	1.17
C_8-diol	1.36	1.95	1.73	1.51	2.20	1.17	1.48
C_8-FFA	0.78	1.26	0.83	1.30	1.22	0.80	0.76
C_{12}	1.06	1.10	1.15	1.05	0.86	1.00	1.07
Trichlorophenol	1.14	1.11	1.41	1.61	1.25	1.29	1.12
Nitrophenol	1.25	0.95	1.28	1.94	1.46	1.50	1.33
C_{18}	1.08	1.20	1.18	1.20	1.21	1.02	1.16
C_{10}	1.10	1.03	1.08	1.05	1.05	1.08	0.91
C_8-NH_2	2.36	7.56	2.00	3.97	3.67	1.79	3.43
C_{12}	1.14	1.08	0.93	1.08	1.07	0.93	1.13
C_{10}-NH_2	1.31	5.23	1.81	2.53	1.53	1.54	1.83
C_{12}-NH_2	1.52	6.73	1.67	1.69	2.24	1.40	1.47
C_{18}	0.88	1.16	0.97	1.05	1.07	0.76	1.08

* $A_s = \frac{a + b}{(a + b) - (b - a)}$, where a is the front half and b the back half of the peak, measured from the perpendicular drawn through the peak maximum[34].

TABLE V

PEAK AREA RATIOS* FOR VARIOUSLY CROSS-LINKED SE-54 COLUMNS

Test compound	*Cross-linking procedures*						
	Uncross-linked	*BP (0.25%) 135°C, 15 min*	*DCBP (0.38%) 150°C, 120 min*	*DCP (0.28%) 175°C, 15 min*	*TBP 165°C, 120 min*	*TBP 220°C, 20 min*	*ATB 220°C, 15 min*
C_{10}	0.98	0.94	0.96	0.86	0.89	0.95	0.94
C_8-OH	1.74	1.72	1.74	1.57	1.65	1.71	1.75
C_8-diol	0.96	1.00	0.88	0.84	0.94	0.84	0.94
C_8-FFA	0.40	0.56	0.39	0.58	0.55	0.39	0.69
C_{12}	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Trichlorophenol	0.73	0.75	0.71	0.63	0.71	0.65	0.76
Nitrophenol	0.96	1.04	0.80	0.82	0.94	0.65	0.98
C_{18}	0.97	0.95	0.93	0.89	0.91	0.97	0.94
C_{10}	0.97	0.97	0.98	0.99	0.96	0.99	0.99
C_8-NH_2	1.07	0.20	0.30	0.78	0.51	0.77	0.87
C_{12}	1.00	1.00	1.00	1.00	1.00	1.00	1.00
C_{10}-NH_2	1.54	0.36	0.39	1.15	0.65	0.97	1.30
C_{12}-NH_2	1.39	0.28	0.26	1.09	0.49	0.47	1.05
C_{18}	0.26	0.15	0.16	0.14	0.42	0.11	0.22

* Peak areas normalized to the dodecane peak area in each of the test mixtures.

were detected with the alkyl amines. For the BP column, 80% of the octylamine was completely and irreversibly adsorbed. Similarly, although the peak symmetry for octylamine on the DCBP column was excellent (2.00), 70% of the compound was totally adsorbed. Consequently, it is necessary to consider both factors when evaluating column inertness. Although the effects of each free radical generator were slightly different for the individual test components, it appears that ATB had overall fewer deleterious effects on the activity and polarity of cross-linked SE-54 stationary phase.

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