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## POLYSILOXANE STATIONARY PHASES CONTAINING TOLYL AND CYANOPROPYL GROUPS: OXIDATION DURING CROSS-LINKING

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### SUMMARY

The majority of studies on non-extractable stationary phases have been done using the methylsilicones. However, there is a need for non-extractable phases containing different functional groups, such as phenyl and cyanopropyl. Tollyl groups have been incorporated into these stationary phases to facilitate free-radical cross-linking. However, it was found that tolyl and cyanopropyl groups can be oxidized during curing with peroxides, producing stationary phase films that are active and thermally unstable. If, on the other hand, azo compounds are used as the free radical generators, these problems are avoided.

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### INTRODUCTION

Considerable effort has been devoted to the immobilization of stationary phases by cross-linking, using peroxides and azo compounds as free-radical generators<sup>1-8</sup>. This cross-linking enhances the thermal stability and non-extractability of these stationary phases.

Film stabilization by cross-linking is even more necessary for phases containing groups other than methyl, because of the large dependence of the viscosity of these polysiloxane polymers on temperature<sup>9</sup>. Initial efforts to stabilize phenyl-containing phases with free radical cross-linking to produce efficient columns were not completely successful, because phenyl groups inhibit cross-linking<sup>1,2</sup>. Peaden *et al.*<sup>10</sup> reported the synthesis of 50% and 70% phenyl polysiloxane phases, which were more viscous than commercially available phases and contained vinyl groups to facilitate *in situ* free-radical cross-linking with peroxides to produce thermally stable and efficient films.

The incorporation of tolyl groups in polysiloxane polymers for cross-linking has been reported by Blomberg and co-workers<sup>11,12</sup>. They prepared a 50% tolyl polysiloxane phase which required lower levels of peroxides than a 50% phenyl polysiloxane. They also synthesized several cyanopropyl silicone gums, containing vinyl or tolyl groups.

In this paper, the synthesis of 50% and 70% tolyl polysiloxanes and of cyanopropyl polysiloxanes, containing vinyl and tolyl groups, is outlined. The *in situ* free-radical cross-linking of these polymers with dicumyl peroxide and azo compounds, and the thermal stability of the resultant silicone rubbers are discussed.

## EXPERIMENTAL

The following silanes were used for the synthesis of the polysiloxane stationary phases: bis(3-cyanopropyl)dichlorosilane, *p*-tolylmethylchlorosilane, vinylmethylchlorosilane, 1,4-dimethyl-1,1,4,4-tetrachlorodisilylethylene, methylphenyldichlorosilane (all from Petrarch Systems, Bristol, PA, U.S.A.) and di-*p*-tolylchlorosilane.

Di-*p*-tolylchlorosilane was synthesized by preparing an ether solution of *p*-tolylmagnesium bromide from equal molar quantities of magnesium and *p*-bromotoluene, according to Pink and Kipping<sup>13</sup>. This solution was slowly added to a rapidly stirred mixture of *p*-tolyltrichlorosilane (Petrarch) and anhydrous diethyl ether at room temperature in a nitrogen atmosphere. The mixture was refluxed for 4–5 h. After it had cooled, the mixture contained a fine white precipitate, which was filtered and washed with anhydrous diethyl ether. The filtrate was concentrated under vacuum and purified by repeated vacuum distillation. The identity and purity of the product were confirmed by nuclear magnetic resonance, boiling point data and gas chromatographic (GC) analysis.

Synthesis of the polymers was accomplished by preparing mixtures of the appropriate chlorosilanes to give the desired composition to the final polymer. The chlorosilane mixtures were dissolved in twice the volume of acetonitrile, placed in an ice-bath and hydrolyzed by the slow additional of a 1:1 mixture of deionized water and acetonitrile until a two-fold excess volume had been added. (For the cyano polymers, the silane mixture was added to the water–acetonitrile mixture to prevent the hydrolysis of the cyano group. The mixtures were allowed to stand for 30 min to ensure reaction completeness. Methylene chloride was added (approximately twice the volume of the original chlorosilanes) to dissolve the siloxanes formed during hydrolysis. The methylene chloride layer was extensively washed with separate portions of deionized water for complete removal of hydrochloric acid. The methylene chloride was finally removed under a nitrogen stream or in a rotary evaporator.

The siloxanes were polymerized by adding tetramethylammonium hydroxide (0.05%, w/w, final concentration) and heating at either 110°C (tolyl) or 125°C (cyanopropyl) for 30 to 90 min under a nitrogen stream after programming from 40°C at either 0.5 or 4°C min<sup>-1</sup>. After polymerization, the polymer was rapidly cooled to room temperature and dissolved in methylene chloride. For end-capping, vinyltrimethylchlorosilane (Petrarch) and 1,3-divinyltetramethyldisilazane (Petrarch) were used at 65°C for 18–22 h.

After end-capping, the methylene chloride solution was extensively washed to ensure a clean polymer. For fractionation, methylene chloride and methanol (tolyl) or acetone and water (cyanopropyl) were used to remove the low-molecular-weight material. The polymer was dried in a vacuum oven to remove the remaining solvent.

Capillary columns (12 m, film thickness 0.25 μm) were prepared by statically coating untreated fused-silica capillary tubing (0.31 mm I.D.; Hewlett-Packard, Avondale, PA, U.S.A.). Coating solutions of the polymers were prepared by dissolving 3.20 mg ml<sup>-1</sup> in purified methylene chloride. Dicumyl peroxide (DCP) (Lucidol Pennwalt, Buffalo, NY, U.S.A.), azo-*tert*.-butane (ATB) (Alfa Products, Danvers, MA, U.S.A.) and azo-*tert*.-octane (ATO)<sup>8</sup> were used for cross-linking.

The column coating solutions were doped with DCP and ATO 30 min prior to use. The concentration varied between 1 and 10% (w/w), depending on the polymer.

After coating, the columns were purged with nitrogen, their ends were sealed in a flame and they were cured at 175°C for 60 min after programming from 40°C at 4°C min<sup>-1</sup> for DCP, and at 150°C for 2 h after programming from 40°C at 10°C min<sup>-1</sup> for ATO. After curing, the columns were washed with approximately 15 ml of methylene chloride for a period of approximately 30 min, and conditioned for 10–12 h before use. In order to calculate the stationary phase loss, a number of columns were conditioned and tested prior to solvent washing.

When ATB was used as the free-radical generator, the columns were first coated. The stationary phase was then saturated with ATB vapors by bubbling nitrogen through ATB and purging the columns for 1 h at 25°C. The columns were sealed immediately after being disconnected from the bubbler and were cured at 220°C for 60 min after programming from 40°C at 10°C min<sup>-1</sup>. After curing, the columns were washed and conditioned as previously described. Several of these columns were also evaluated prior to and after solvent washing in order to calculate the stationary phase loss.

Column evaluations were accomplished using a Carlo Erba 4160 Fractovap gas chromatograph, equipped with an on-column injector and flame ionization detector. Hydrogen was used as carrier gas at a linear velocity between 50 and 100 cm sec<sup>-1</sup>. The oven was programmed from the starting temperature at 4°C min<sup>-1</sup> to the upper temperature after a 2-min isothermal period. The sensitivity was set to give a full-scale peak for 1 ng of *n*-dodecane.

## RESULTS AND DISCUSSION

As previously mentioned, the presence of phenyl groups in polysiloxanes inhibits free-radical cross-linking. This can be overcome by incorporating vinyl groups into the polymer; however, high concentrations of peroxide (3–10%, depending on the phenyl content of the polymer) are needed<sup>9,10</sup>.

TABLE I  
LOSS OF STATIONARY PHASE AFTER CROSS-LINKING AND SOLVENT WASHING

<i>Stationary phase</i>	<i>Cross-linking agent</i>	<i>Washout (%)</i>
50% Tolyl	1.0% DCP	5
50% Phenyl*	1.0% DCP	90
50% Phenyl*	3.5% DCP	12
70% Tolyl	4.0% DCP	10
70% Phenyl**	10.0% DCP	5
50% Tolyl	ATB	6
70% Tolyl	ATB	7
50% Phenyl*	ATB	6
90% Cyanopropyl***	ATB	9
90% Cyanopropyl***	3.5% ATO	10

\* 50% Phenyl, 1% vinyl, 49% methyl.

\*\* 70% Phenyl, 4% vinyl, 26% methyl.

\*\*\* 90% Cyanopropyl, 10% tolyl.

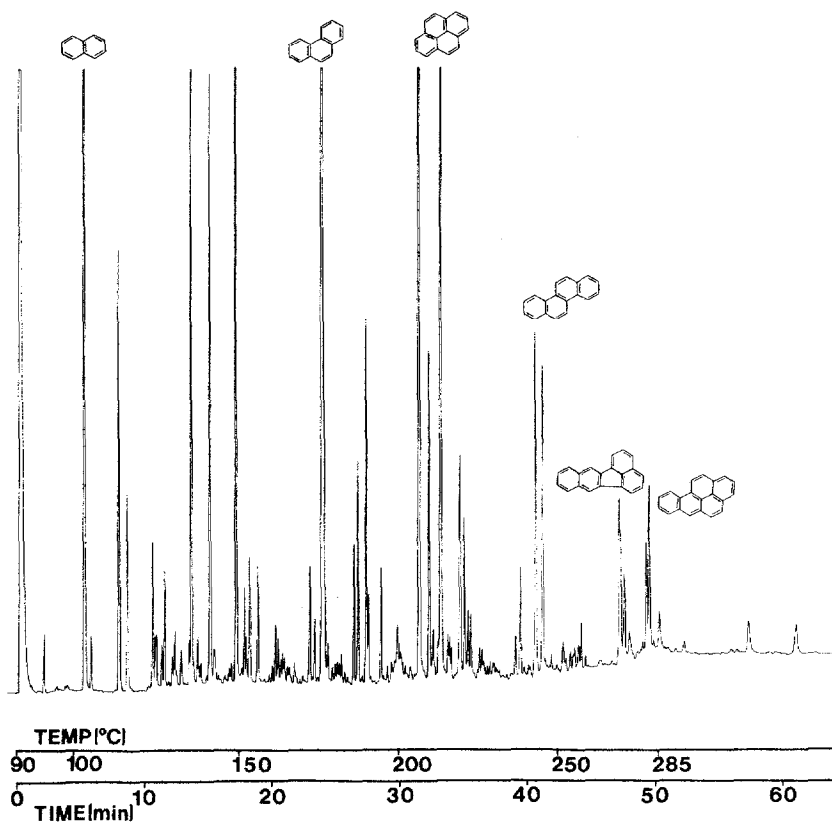


Fig. 1. Gas chromatogram of a coal tar. Conditions: 12 m  $\times$  0.31 mm fused-silica column; 70% tolyl polysiloxane stationary phase (0.25- $\mu$ m film thickness) cross-linked with ATB; temperature program from 90 to 285°C at 4°C min<sup>-1</sup> after a 2-min isothermal period; H<sub>2</sub> carrier gas at 75 cm sec<sup>-1</sup>.

The use of tolyl groups instead of phenyl groups permits cross-linking with lower peroxide levels. GC measurements of the capacity ratios,  $k'$ , of *n*-decane, *n*-undecane and *n*-dodecane at 60°C were made both before and after solvent washing of the prepared columns. The results are summarized in Table I.

Fig. 1 shows a typical chromatogram of a coal tar, obtained on an ATB-cross-linked 70% tolyl polysiloxane stationary phase. As can be seen, this polymer produces a highly efficient stationary phase when cross-linked on fused silica.

Tolyl groups can be incorporated, as well, into other polysiloxane polymers for cross-linking. A 50% phenyl polymer containing 1% tolyl can cross-link easier (higher level of non-extractability) than a 50% phenyl polymer containing 1% vinyl with the same level of peroxide. Tolyl groups also cross-link more easily in cyano polysiloxane polymers than do vinyl groups. Fig. 2 shows a typical chromatogram on a 90% cyanopropyl, 10% tolyl polysiloxane stationary phase. A comparison of  $k'$  values shows a loss of approximately 9% of the phase after solvent washing. Figs. 3 and 4 give a comparison of the selectivity of this phase to that of a 50% phenyl polysiloxane.

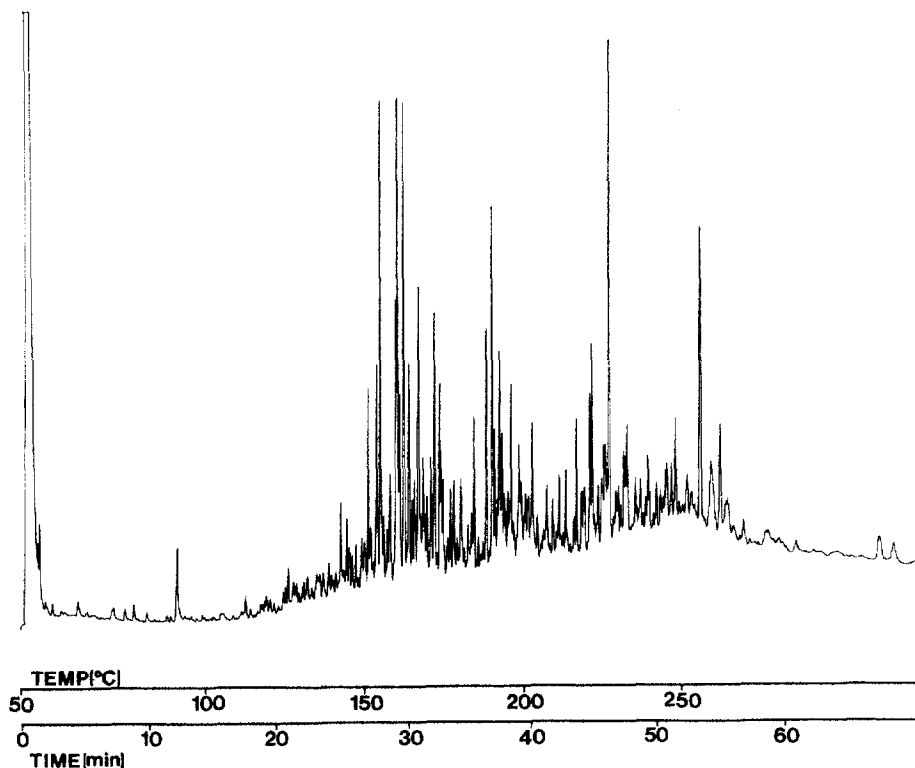


Fig. 2. Gas chromatogram of an amino polycyclic aromatic hydrocarbon fraction of a coal liquid. Conditions: 12 m  $\times$  0.31 mm fused-silica column; 90% cyanopropyl, 10% tolyl polysiloxane stationary phase (0.25- $\mu$ m film thickness) cross-linked with ATB; temperature program from 50 to 250°C at 4°C min<sup>-1</sup> after a 2-min isothermal period; H<sub>2</sub> carrier gas at 75 cm sec<sup>-1</sup>.

Although the use of tolyl groups in polysiloxane polymers allows cross-linking to take place more easily, several problems were observed. When a column which had been coated with the 50% tolyl polymer and cross-linked with DCP was allowed to remain unsealed on the lab bench for 2 weeks and then re-evaluated, an increase in activity and column bleed, and a decrease in efficiency were observed. It was also found that the tolyl polymer was more stable when cross-linked with ATB than with DCP. Even though work in this laboratory has shown that a cross-linked 70% phenyl polysiloxane stationary phase can be used up to 400°C<sup>10</sup>, the same was not true of the 70% tolyl polysiloxane polymer.

Therefore, several polymers were subjected to various conditions and analyzed by infrared (IR) spectroscopy in order to evaluate their chemical stability. When a 50% tolyl polysiloxane polymer was heated at 175°C in air, an absorption band appeared in the IR spectrum at 1700 cm<sup>-1</sup>, indicating the presence of carbonyl groups caused by the oxidation of the tolyl functionality. The polymer was also discolored. If the polymer was heated to 175°C in the absence of oxygen, no carbonyl stretching band appeared (see Fig. 5A).

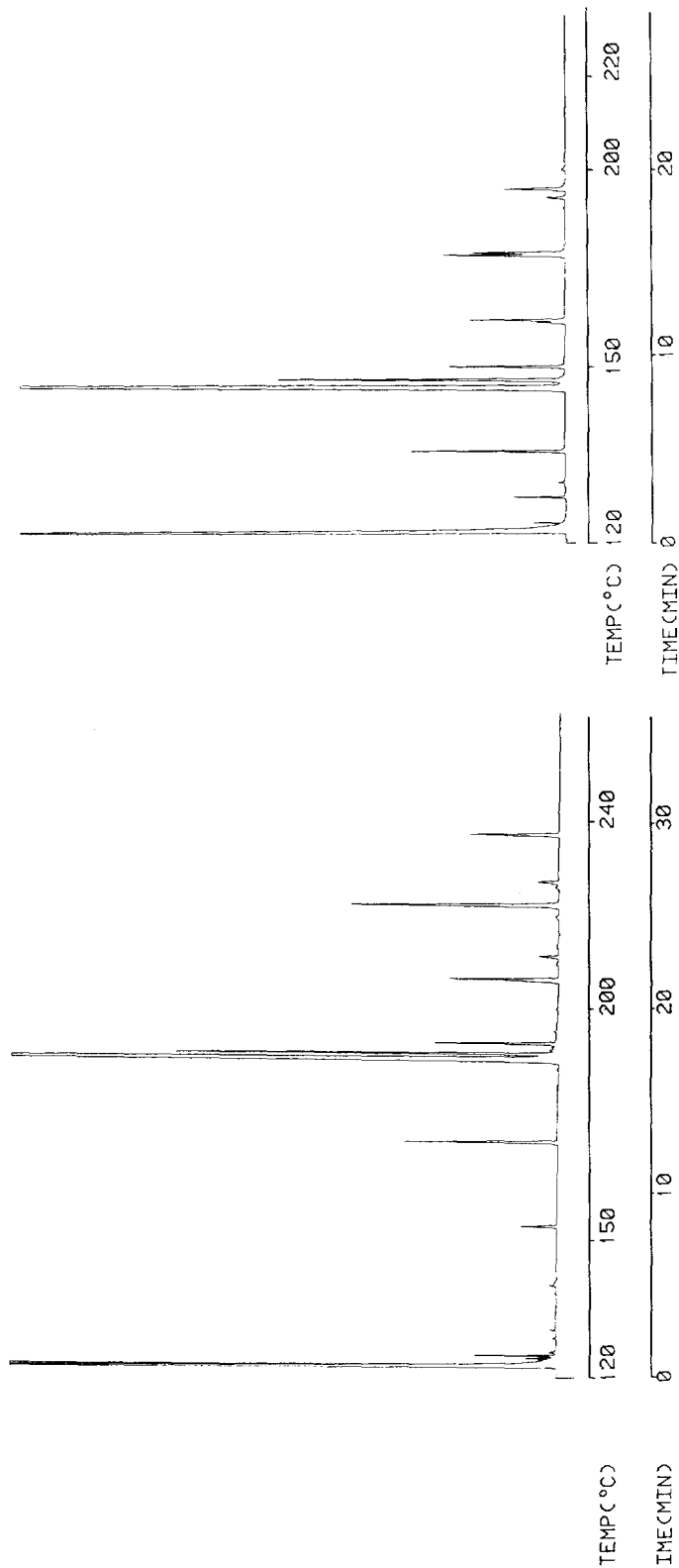


Fig. 3. Gas chromatogram of fatty acid methyl esters. Conditions: 12 m  $\times$  0.31 mm fused-silica column; 50% phenyl, 1% vinyl polysiloxane stationary phase (0.25- $\mu$ m film thickness) cross-linked with ATB; temperature program 120 to 140°C at 4°C min<sup>-1</sup> after a 2-min isothermal period; H<sub>2</sub> carrier gas at 75 cm sec<sup>-1</sup>.

Fig. 4. Gas chromatogram of fatty acid methyl esters. Conditions: 12 m  $\times$  0.31 mm fused-silica column; 90% cyano, 10% tolyl polysiloxane stationary phase (0.25- $\mu$ m film thickness) cross-linked with ATB; temperature program from 120 to 220°C at 4°C min<sup>-1</sup> after a 2-min isothermal period; H<sub>2</sub> carrier gas at 75 cm sec<sup>-1</sup>.

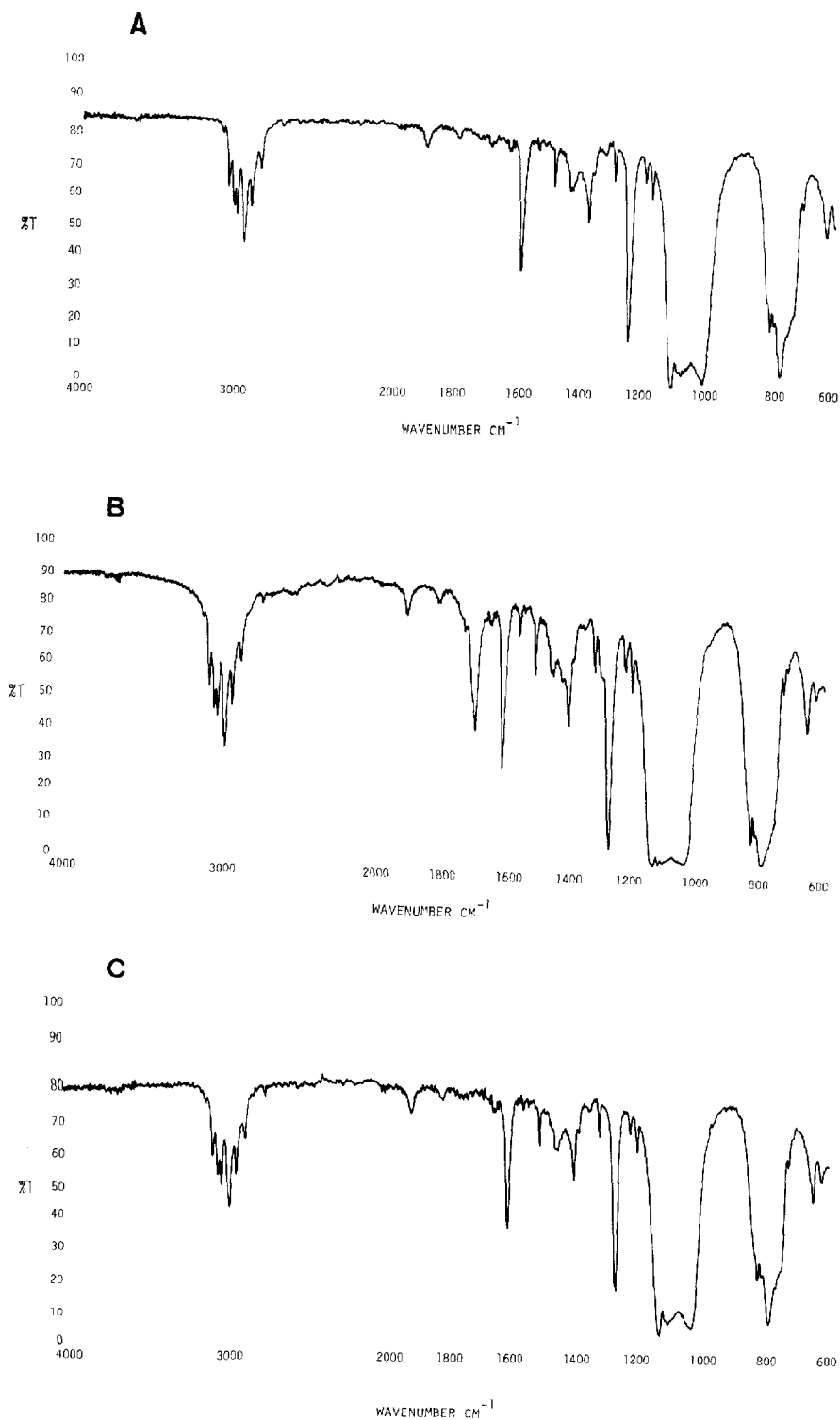


Fig. 5. IR spectra of 50% tolyl polysiloxane stationary phase: A, heated at 175°C for 1 h under dry nitrogen; B, heated at 175°C for 1 h under dry nitrogen, doped with DCP (≈ 5%, w/w); C, heated at 220°C for 1 h under dry nitrogen, doped with ATB (≈ 5%, w/w).

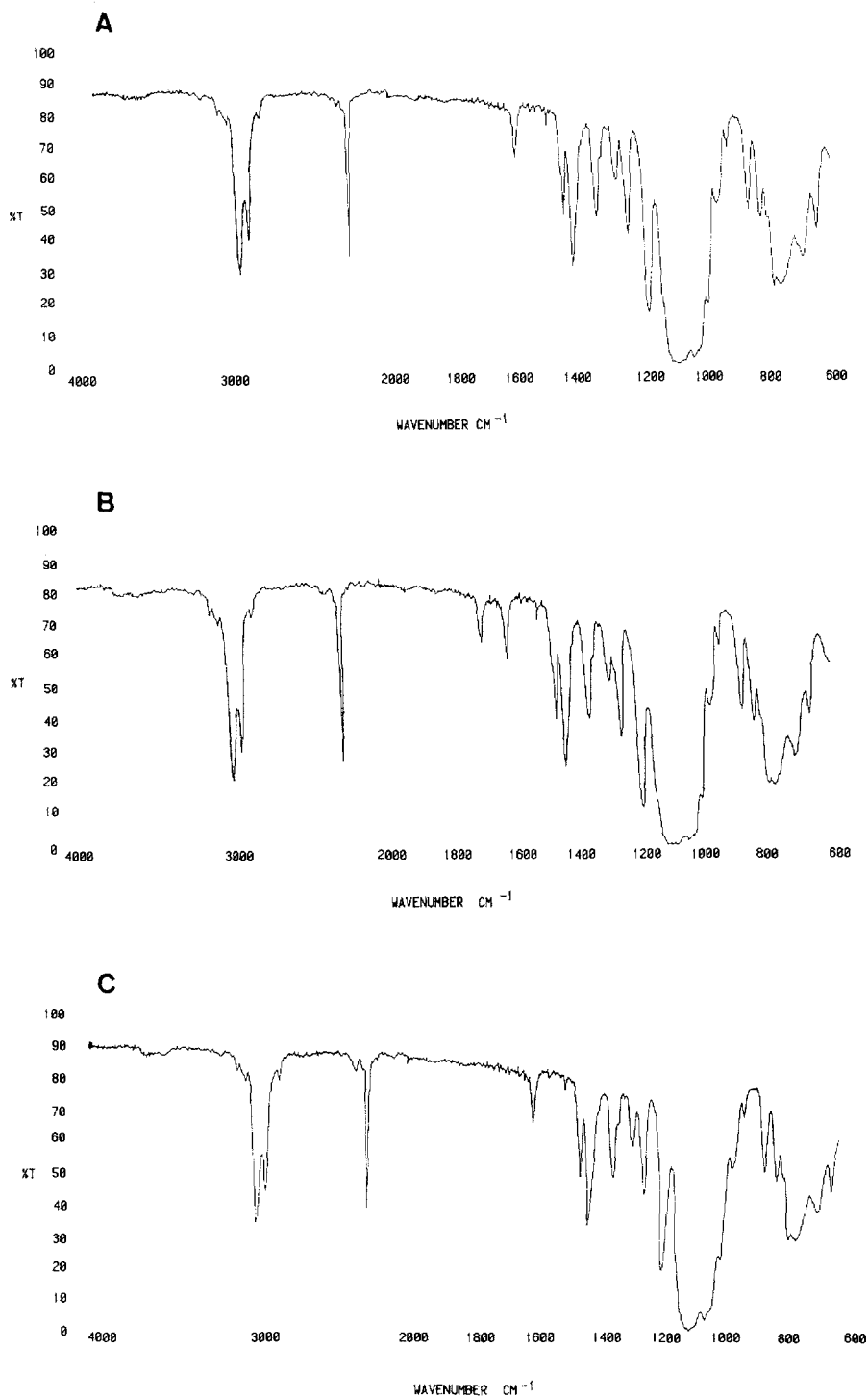


Fig. 6. IR spectra of 90% cyano, 10% tolyl polysiloxane stationary phase: A, heated at 175°C for 1 h under dry nitrogen; B, heated at 175°C for 1 h under dry nitrogen, doped with DCP (≈ 5%, w/w); C, heated at 150°C for 2 h under dry nitrogen, doped with ATO (≈ 5%, w/w).



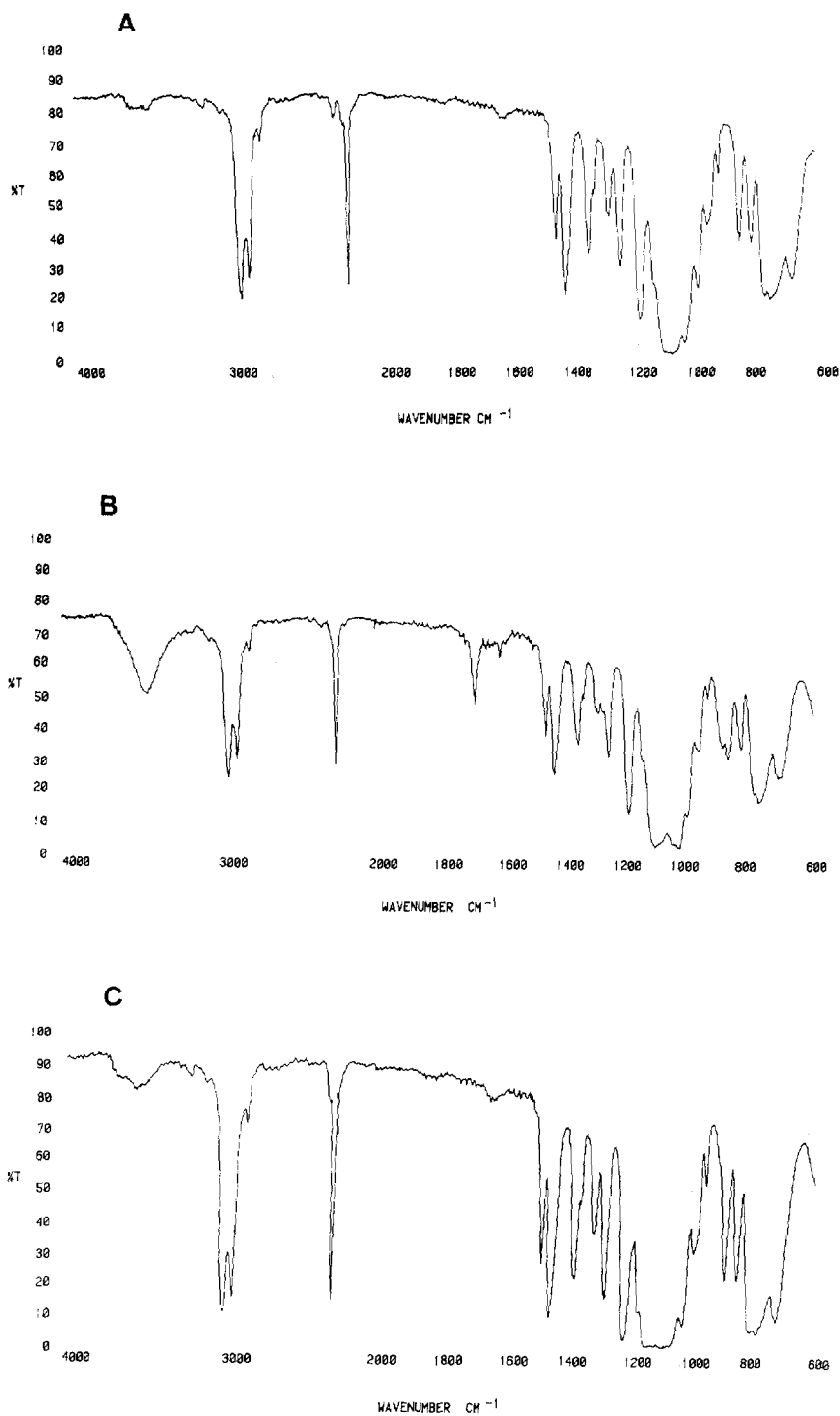


Fig. 7. IR spectra of Silar 10C: A, heated at 175°C for 1 h under dry nitrogen; B, heated at 175°C for 1 h under dry nitrogen, doped with DCP ( $\approx 5\%$ , w/w); C, heated at 150°C for 1 h under dry nitrogen, doped with ATO ( $\approx 5\%$ , w/w).

When the tolyl polymer was doped with DCP ( $\approx 5\%$ , w/w) and heated to  $175^\circ\text{C}$  in an inert atmosphere, the carbonyl band also appeared (see Fig. 5B). Apparently, oxygen that is produced during the decomposition of DCP causes oxidation of some tolyl groups in the polymer. However, when ATB was added to the polymer before heating to  $220^\circ\text{C}$  under dry nitrogen, no carbonyl band was seen in the IR spectrum, as shown in Fig. 5C.

Similar results were obtained when a 90% cyanopropyl, 10% tolyl polysiloxane polymer was used (Fig. 6). Oxidation of this polymer occurred when doped with DCP and heated at  $175^\circ\text{C}$  under dry nitrogen; however, none occurred when ATO was used. In order to determine whether the observed oxidation took place on the tolyl or cyanopropyl group of this cyanopropyl/tolyl polymer, the same tests were conducted with Silar 10C (100% cyanopropyl). DCP caused oxidation of this polymer as well: ATO did not (Fig. 7).

From these studies, it is clear that even though tolyl groups do facilitate free-radical cross-linking, they are also easily oxidized. Cyanopropyl groups can also be oxidized when cross-linked with peroxides.

The use of DCP as well as other peroxides, for free-radical cross-linking should be reassessed. Oxygen is produced by the thermal decomposition of peroxides which can lead to oxidation of susceptible stationary phases, as is seen with the tolyl and cyanopropyl phases. This oxidation tends to produce active columns and degradation of the polysiloxane phases. On the other hand, it has been shown that ATB and ATO easily cross-link stationary phases that range from methyl to cyanopropyl in polarity, causing no activity problems or oxidation of the polymers<sup>8</sup>. It is possible, using ATB or ATO, to prepare non-extractable stationary phases from polymers containing reactive groups, such as tolyl or cyanopropyl, which are thermally stable, provided that great care is taken to exclude oxygen from the carrier gas.

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#### REFERENCES

- 1 K. Grob, G. Grob and K. Grob, Jr., *J. Chromatogr.*, 211 (1981) 243.
- 2 K. Grob and G. Grob, *J. Chromatogr.*, 213 (1981) 211.
- 3 K. Grob and G. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 491.
- 4 K. Grob and G. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 13.
- 5 P. Sandra, G. Redant, E. Schodt and M. Verzele, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 411.
- 6 B. W. Wright, P. A. Peaden, M. L. Lee and T. J. Stark, *J. Chromatogr.*, 248 (1982) 17.
- 7 L. Blomberg, J. Buijten, K. Markides and T. Wännman, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 578.
- 8 B. E. Richter, J. C. Kuei, N. J. Park, S. J. Crowley, J. S. Bradshaw and M. L. Lee, *J. High. Resolut. Chromatogr. Chromatogr. Commun.*, in press.
- 9 B. W. Wright, P. A. Peaden and M. L. Lee, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 413.
- 10 P. A. Peaden, B. W. Wright and M. L. Lee, *Chromatographia*, 15 (1982) 335.
- 11 J. Buijten, L. Blomberg, K. Markides and T. Wännman, *Chromatographia*, 16 (1982) 183.
- 12 K. Markides, L. Blomberg, J. Buijten and T. Wännman, *J. Chromatogr.*, 254 (1983) 53.
- 13 H. S. Pink and F. S. Kipping, *J. Chem. Soc. (London)*, 123 (1982) 2830.