Low-molecular polyethylene — low-polar high-temperature stationary phase for gas chromatography

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Received 14 January 1981

The properties of low-molecular polyethylene as stationary phase for gas chromatography are described. The resolving properties are characterized by retention indices of the standards according to McReynolds as well as the standards proposed for higher temperatures. The original sample of the low-molecular polyethylene as well as its extracted portion may be used up to 300°C. Some examples of the application of these phases are presented.

В работе описываются свойства низкомолекулярного полиэтилена как неподвижной фазы при газовой хроматографии. Разделительная способность характеризуется показателями задержки стандартов по Макрейнольдсу и стандартов, предложенных для более высоких температур. Оригинальные образцы низкомолекулярного полиэтилена и экстрагированную долю из него можно использовать до 300°C. Приводится несколько примеров использования этих фаз.

Up to the present, more than 1100 substances were used as stationary phases in gas chromatography. This great number was not providing an easy survey for selection of the optimum stationary phase and, for this reason, some authors suggested to reduce this number to six or twelve [1—3]. On the other hand, other authors put forward various classification systems which should facilitate the orientation in the choice of the most convenient stationary phase [4—12]. In spite of these tendencies, the development did not come to a stop. New stationary phases come into use and, in many cases, they exhibit high-selective properties or high temperature stability [13].

However, there are only 5% of nonpolar phases in this great number of substances used. It is characteristic of these nonpolar substances that only one kind of interaction forces, *i.e.* dispersion forces, is in operation in the course of separation.

The large majority of these nonpolar phases are substances with relatively low boiling points and may be therefore used up to 200°C at most. The substances which may be also used above this temperature, for instance paraffins [14—21], paraffinic mixtures [22—24], mineral oils [25, 26], distillation residues of crude petroleum [27] or asphalt [28, 29] represent only 1% of these nonpolar phases. None of these substances came into wider use.

Some authors also attempted to use polyolefins as stationary phases [30]. Polyethylene of high molecular weight is not usable as a stationary phase [31, 32]. On the other hand, the ethylene—propylene copolymer was suited to the analysis of the products of pyrolysis [33, 34]. Polybutene was applied to the analysis of insecticides [35].

Riedo and coworkers [36] prepared by complicated synthesis the hydrocarbon $C_{87}H_{176}$ which could be used up to 300°C. Its resolving properties were tested by *Haken* and *Ho* [37] and by *Soják et al.* [38] in a capillary column. *Vernon* and *Ogundipe* [39] recommend the hydrogenated Apiezon M for high temperatures.

Apiezons, especially Apiezon L, and silicone elastomers are frequently put into the class of nonpolar phases. Apiezon L, which is similar to other Apiezons as concerns the resolving properties [40], is not quite nonpolar because it contains unsaturated bonds. This fact sometimes brings about an increase in retention times (Table 3). The silicone elastomers often exhibit different resolving properties with respect to stationary phases of the hydrocarbon type because of different properties of the silicon and carbon atom.

The production of low-density polyethylene gives rise to low-molecular portions as by-products. We used this substance for chromatographic separation of polyethylene glycols and ethoxylated derivatives with relatively good results [41]. Therefore we tested the resolving properties and possibility of using this substance as a nonpolar stationary phase in more detail.

Experimental

The experiments were performed with a chromatograph HP 5830 A (Hewlett—Packard, Palo Alto, California) equipped with a flame ionization detector. The lengths of the metallic columns with internal diameter of 3 mm changed from 1.0 to 2.5 m. In all cases, we used Chromaton N-AW-HMDS, size 0.16—0.20 mm (Lachema, Brno) as a carrier.

Physical properties of the low-molecular polyethylene and of the fraction prepared from this substance

The low-molecular polyethylene (PE) (product of Slovnaft, Bratislava) is a viscous colourless substance soluble in warm *o*-dichlorobenzene. Its solubility in current organic solvents is limited. According to the results obtained by ^{13}C-n.m.r. spectroscopy, branched hydrocarbons of all possible types are present in this substance. Moreover, it also contains small amount of double bonds.

Table 1

Physical constants of the low-molecular PE and Vupol 2000

Physical property	Low-molecular PE	Vupol 2000
Molecular weight	—	2040
Distribution of molecular weights (GPC method)	—	1120—4500
Density 70/4°; ϱ/g cm^{-3}	0.825	0.823
Volume expansion coefficient/K^{-1}	0.0006	0.0006
Viscosity/mPa s (85°C)	1900	491
Acidity number, mg KOH g^{-1}	0.1	0.1
Bromine number, g Br/100 g	3.1	2.0
Index of refraction, n_D^{20}	1.488	1.484
Content of CH_3 groups, %	22	20
Ash content/mass %	1×10^{-3}	1×10^{-4}

By dissolving the low-molecular PE in benzene, centrifuging the insoluble portion, and evaporating the solvent, we prepared a fraction with narrower molecular weight distribution. We named it Vupol 2000. Some physical constants of both substances are given in Table 1.

The mass loss of both substances was measured in the temperature interval 200—300°C by thermogravimetric analysis (TGA) as well as by dynamic method. The working procedure for the dynamic method is as follows. A sample of Vupol 2000 or low-molecular PE is heated in a flask to 200, 250, and lastly to 300°C and simultaneously nitrogen is supplied from a pressure gas vessel into the flask. The mass loss was determined by weighing after each two hours of bubbling. The data in Table 2 evidence that the mass losses of both samples decreased to a passable [42] value, *i.e.* 0.03 mg per 1 l of nitrogen. As the mass loss gets on with time, it may be expected that it will still decrease with continuing bubbling. It results from the measured data that either substance may be used up to 300°C and for a short time even to still higher temperatures.

Resolving properties of the low-molecular PE and Vupol 2000

The resolving properties with respect to n-paraffins are characterized by the slope of the linear relationship between the logarithm of value of pure retention time and the number of carbon atoms in n-paraffin. The values of the slope for the low-molecular PE and Vupol 2000 at 120°C are 0.3131 and 0.2857, respectively. *McReynolds* [5] gives the value 0.2891 for squalane. The higher value of the slope

Table 2

Mass loss of the low-molecular PE and Vupol 2000
at the temperatures 200—300°C

Time of bubbling t/h	Loss					
	Dynamic method				TGA analysis	
	Low-molecular PE		Vupol 2000		Low-molecular PE	Vupol 2000
	%	mg dm^{-3}	%	mg dm^{-3}	%	%
	200°C				2.63	2.87
2	1.65	0.35	0.61	0.16		
4	2.55	0.22	1.39	0.19		
6	2.68	0.03	1.49	0.03		
	250°C				3.14	3.28
2	3.12	0.10	1.69	0.05		
4	3.35	0.06	1.88	0.05		
6	3.44	0.02	2.18	0.03		
	300°C				3.64	3.72
2	3.77	0.08	3.05	0.20		
4	3.89	0.03	3.37	0.12		
6	3.97	0.00	3.52	0.02		

on the low-molecular PE means that the difference between the retention times of two successive n-alkanes will be the greatest on this stationary phase. The near values of the slopes for Vupol 2000 and squalane point to similar properties of these two stationary phases. Similar conclusions may be also drawn from the relationship between the logarithm of value of pure retention time and the boiling point of n-paraffins (Fig. 1). The slopes of linear relations are 0.0107 for Vupol 2000 and 0.0114 for the low-molecular PE. *Purnell* gives the value 0.0115 for squalane [43]. From the course of relationships for the low-molecular PE and Vupol 2000, we could infer that higher (C_9 and more) n-paraffins should be better separated on the low-molecular PE. As the width of waves of n-paraffins on this phase is also larger, the real resolution power of both these stationary phases is equal.

The resolving properties with respect to linear 1-olefins expressed by retention indices are quoted in Table 3. For comparison, we give the retention indices of

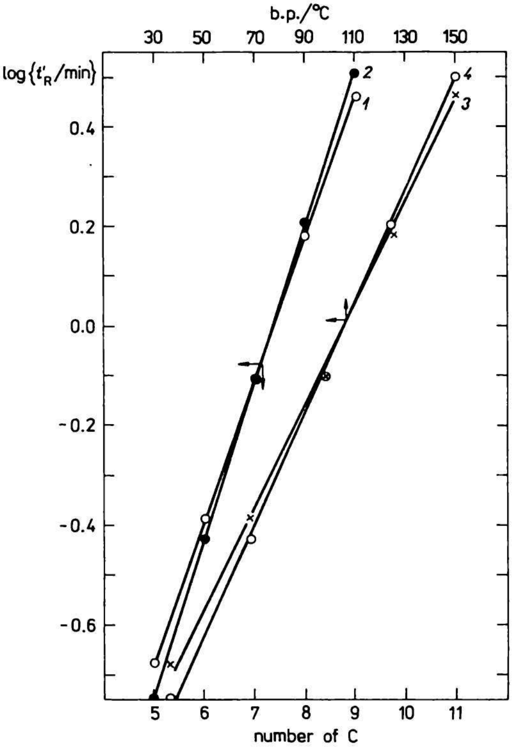

Fig. 1. Variation of the logarithm of value of retention time (log t'_R/min) with the number of carbon atoms in n-paraffins (C) and with their boiling point values.

Conditions: 10% of stationary phase, length of column 2.5 m, diameter 3 mm, temperature of column 120°C, flow of nitrogen 24 $cm^3 min^{-1}$.

1. log t'_R/min — C on Vupol 2000; *2.* log t'_R/min — C on the low-molecular PE; *3.* log t'_R/min — boiling point/°C on Vupol 2000; *4.* log t'_R/min — boiling point/°C on the low-molecular PE.

Table 3

Retention indices (*I*) of linear 1-olefins on Vupol 2000 and other low-molecular stationary phases
Conditions: 5% of stationary phase, temperature of column 140°C,
length of column 2.5 m, flow of nitrogen 24 $cm^3 min^{-1}$

1-Olefin	Vupol 2000	Squalane	SE-30	Apiezon L
		I		
C_{10}	980	986	1000	1017
C_{11}	1079	1084	1100	1118
C_{12}	1180	1184	1200	1216
C_{13}	1280	1285	1300	1314
C_{14}	1380	1384	1400	1416

these olefins on other stationary phases of low polarity as well. The values of retention indices on poly(dimethylsiloxane) SE-30 which has been proposed as basic stationary phase are interesting. The measured values show that the sp^3 hybridized atoms of silicon as Lewis acids form weak complexes with the π bonds of olefins owing to which the retention indices of olefins are greater. The retention indices of olefins on Apiezon L are still greater because of interaction of the unsaturated bonds in this stationary phase.

The polarity of the low-molecular PE and Vupol 2000 was characterized by the values of retention indices of the McReynolds standards. The results are summarized in Table 4. For comparison, we quote the values of retention indices of other nonpolar stationary phases as well. The retention indices of polar standards on the low-molecular PE and Vupol 2000 are higher than on squalane, which evidences an interaction of these stationary phases with polar functional groups. Both these substances contain unsaturated bonds. This increased interaction is due not only to the present double bonds but also to rich branching of the hydrocarbon chain, as proved by *Kemenade* and *Groenendijk* [21].

Table 4

Retention indices (I) of the McReynolds standards on the low-molecular PE
and Vupol 2000 and other nonpolar stationary phases
Conditions: 10% of stationary phase, length of column 2.5 m,
temperature of column 120°C, flow of nitrogen 27 cm^3 min^{-1}

Standard	Benzene	Butanol	2-Pentanone	1-Nitropropane	Pyridine
Stationary phase			I		
Low-molecular PE	676	622	639	692	754
Vupol 2000	642	612	629	684	745
Apiezon M-H [24]	671	599	632	667	736
Squalane [20]	653	590	627	652	699
$C_{87}H_{176}$ [23]	674	600	630	664	724
Copolymer Ethylene-propylene [20]	684	601	636	675	733

In order to characterize the resolving properties at higher temperatures, we measured the retention indices of standards, proposed by *Vernon et al.* [44]. These values are listed in Table 5. For comparison, we give the retention indices on hydrogenated Apiezon M according to literature as well. The differences between the values of indices on all three stationary phases are not significant and are caused rather by experimental errors than interactions between stationary phases and analyzed substances.

Table 5

Retention indices (I) of standards for higher temperatures on the low-molecular PE and Vupol 2000
Conditions: 10% of stationary phase, length of column 2.5 m, temperature of column 180°C, flow of nitrogen 27 cm^3 min^{-1}

Standard	Butylbenzene	Octanol	2-Octanone	1-Nitrohexane	Symmetric collidine
Stationary phase			I		
Low-molecular PE	1076	996	936	982	1008
Vupol 2000	1098	1042	958	1016	1033
Apiezon M-H [29]	1085	954	942	988	1012

Influence of the quantity of stationary phase on the resolving power of column

The optimum quantity of stationary phase was tested with a mixture of n-paraffins and linear 1-olefins C_{10}—C_{13}. We prepared the columns with 5, 10, and 15% (by mass) of Vupol 2000 and observed the resolution of the couple paraffin—olefin (R) as well as the height of theoretical plate (HETP) of olefin C_{12}. We measured the following values: 5% of stationary phase, $R = 1.03$, $\text{HETP}_{\text{min}} = 0.84$ mm; 10% of stationary phase, $R = 1.07$, $\text{HETP}_{\text{min}} = 0.75$ mm; 15% of stationary phase, $R = 0.95$, $\text{HETP}_{\text{min}} = 1.20$ mm. It results from these data that the resolving power of column decreases with increasing percentage of stationary

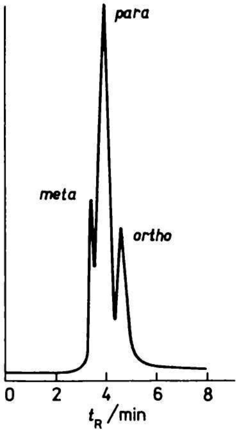

Fig. 2. Chromatogram of xylenes mixture.
Conditions: 10% of Vupol 2000, length of column 1.5 m, temperature 80°C, flow of nitrogen 27 cm^3 min^{-1}.

phase. Analogously, that is also valid for the low-molecular PE. The decrease in power of a column at a higher content of stationary phase is due to increasing value of the term which expresses the influence of the resistance to mass transport from the liquid phase to gaseous phase and *vice versa*. The increase of its value is caused by a relatively high viscosity of both substances.

Some examples of the application of the tested stationary phases are given in Figs. 2—5.

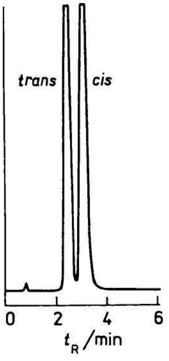

Fig. 3. Chromatogram of *cis* and *trans* decalin.
Conditions: 5% of the low-molecular PE, length of column 1.5 m, temperature of column 140°C, flow of nitrogen 25 cm³ min⁻¹.

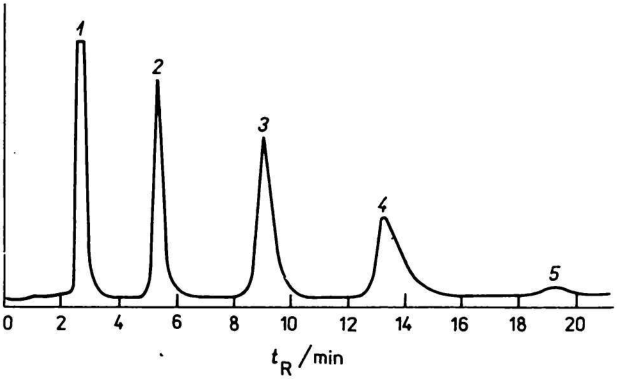

Fig. 4. Chromatogram of monobutyl glycol ethers.
Conditions: 10% of Vupol 2000, length of column 1.5 m, diameter 3 mm, flow of nitrogen 27 $cm^3\ min^{-1}$.
Temperature program: initial temperature 220°C, gradient 5 K min^{-1}, final temperature 280°C.
1. Tetraethylene glycol monobutyl ether; *2*. pentaethylene glycol monobutyl ether; *3*. hexaethylene glycol monobutyl ether; *4*. heptaethylene glycol monobutyl ether; *5*. octaethylene glycol monobutyl ether.

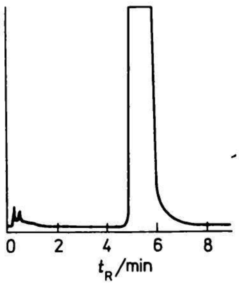

Fig. 5. Chromatogram of squalane.
Conditions: 10% of Vupol 2000, length of column 1 m, diameter 3 mm, temperature 280°C, temperature of sample injector and detector 300°C, flow of nitrogen 27 $cm^3 min^{-1}$.
Injected 2 mm^3 of sample.

Conclusion

The reproducibility of physical properties of both substances was tested with some samples from production practice. The values differed from each other in the range of tolerance usual in chemical production.

The recommended stationary phases possess resolving properties similar to those of hydrogenated Apiezon M. Their drawback is a rather high viscosity. However, their merit consists in the fact that they are easily procurable, which is pretty important for the use of preparative chromatography, especially in industrial laboratories.

It follows from the presented examples that both the tested stationary phases are usable for separation of polar and nonpolar substances which may have a high boiling point.

References

1. Hawkes, S., Grossman, D., Hartkopf, A., Isenhour, T., Leary, J. J., and Parcher, J., *J. Chromatogr. Sci. 13,* 115 (1975).
2. Clutton, D. W., *J. Chromatogr. Sci. 10,* 14A (1977).
3. Delley, R. R. and Friedrich, K., *Chromatographia 10,* 593 (1977).
4. Rohrschneider, L., *Z. Anal. Chem. 170,* 256 (1959).
5. McReynolds, W. O., *J. Chromatogr. Sci. 8,* 685 (1970).
6. Novák, J., Ružičková, J., Wičar, S., and Janák, J., *Anal. Chem. 45,* 1365 (1973).
7. Ashes, J. R., Haken, J. K., and Souter, P., *J. Chromatogr. 92,* 237 (1974).
8. Risby, T. H., Jurs, P. C., and Reinhold, B. L., *J. Chromatogr. 99,* 173 (1974).
9. Hartkopf, A., *J. Chromatogr. Sci. 12,* 119 (1974).
10. Figgins, C. E., Risby, T. H., and Jurs, P. C., *J. Chromatogr. Sci. 14,* 453 (1976).
11. Ettre, L. S., *Chromatographia 7,* 261 (1968).
12. Leary, J. J., Justice, J. B., Tsuge, S., Loury, S. R., and Isenhour, T. L., *J. Chromatogr. Sci. 11,* 201 (1973).
13. Verzele, M. and Sandra, P., *J. Chromatogr. 158,* 111 (1978).
14. Desty, D. H. and Whyman, B. H. F., *Anal. Chem. 29,* 320 (1957).

15. Meyer, R. A., in *Gas Chromatography.* (Coates, V. J., Noebels, H. J., and Fagerson, I. S., Editors.) P. 93. Academic Press, New York, 1958.
16. Kwantes, A. and Rijnders, G. W. A., in *Gas Chromatography.* (Desty, D. H., Editor.) P. H-63. Butterworths, London, 1958.
17. Yasadu, S. K., *J. Chromatogr. 27,* 72 (1967).
18. Keller, R. A., *J. Chromatogr. 5,* 225 (1961).
19. Karger, B. L., Elmerik, Y., and Andrade, W., *J. Chromatogr. Sci. 7,* 209 (1969).
20. Vigdergauz, M. S. and Andreev, L. V., *Zavod. Lab. 31,* 550 (1965).
21. Kemenade, A. W. O. and Groenendijk, H., *Chromatographia 2,* 316 (1969).
22. Desty, D. H., Godfrey, F. M., and Harbourn, C. L. A., in *Gas Chromatography.* (Desty, D. H., Editor.) P. M-111. Butterworths, London, 1958.
23. Pollard, F. H. and Hardy, C. J., in *Gas Chromatography.* (Scott, R. P. W., Editor.) P. 115. Butterworths, London, 1957.
24. Harrison, G. F., in *Gas Chromatography.* (Scott, R. P. W., Editor.) P. 333. Butterworths, London, 1957.
25. Brooks, V. T. and Collins, G. A., *Chem. Ind.* (London) *1956,* 921.
26. Hively, R. A., *J. Chem. Eng. Data 5,* 237 (1960).
27. Zizin, V. G., Ivanova, T. S., and Sokolova, V. I., *Khim. Tekhnol. Topl. Masel,* No. 3, 66 (1969).
28. Böttcher, F. and Meijer, J. W. A., *J. Chromatogr. 6,* 535 (1961).
29. Baumann, F. and Lavigne, J. B., in *Gas Chromatography.* (Fowler, L., Editor.) P. 139. Academic Press, New York, 1963.
30. Onuska, F. I., *J. Chromatogr. 186,* 259 (1979).
31. Keppler, J. G., Dijkstra, G., and Schols, J. A., in *Gas Chromatography.* (Scott, R. P. W., Editor.) P. 222. Butterworths, London, 1957.
32. Bender, G. T. and Meloan, C. E., *J. Chromatogr. 45,* 220 (1969).
33. Bieber, O., Degler, G., and Schnecko, H., *J. Chromatogr. Sci. 7,* 591 (1969).
34. Thizon, M., Eon, C., Valentin, P., and Guiochon, G., *Anal. Chem. 48,* 1861 (1976).
35. Richardson, A., *Chem. Ind.* (London) *1965,* 1337.
36. Riedo, F., Fritz, D., Tarján, G., and Kováts, E., *J. Chromatogr. 126,* 63 (1976).
37. Haken, J. K. and Ho, D. K. M., *J. Chromatogr. 142,* 203 (1977).
38. Soják, L. and Krupčík, J., *J. Chromatogr. 191,* 199 (1980).
39. Vernon, F. and Ogundipe, C. O. E., *J. Chromatogr. 132,* 181 (1977).
40. Castello, G., *J. Chromatogr. 66,* 213 (1972).
41. Šingliar, M. and Macho, V., *Petrochémia 19,* 157 (1979).
42. Gerrad, W., Hawkes, S. J., and Mooney, E. F., in *Gas Chromatography.* (Scott, R. P. W., Editor.) P. 263. Butterworths, London, 1960.
43. Purnell, H., *Plynová chromatografia.* (Czech translation.) P. 237. Státní nakladatelství technické literatury. (State Publishing House of Technical Literature.) Prague, 1966.
44. Vernon, F. and Gopal, P. L., *J. Chromatogr. 150,* 45 (1978).

Translated by R. Domanský