

CHROM. 5643

ANTIOXIDANTS AND STABILIZERS. XXXIII. ANALYSIS OF STABILIZERS OF ISOTACTIC POLYPROPYLENE: APPLICATION OF GEL PERMEATION CHROMATOGRAPHY

J. ČOUPEK, S. POKORNÝ, J. PROTIVOVÁ, J. HOLČÍK, M. KARVAŠ AND J. POSPÍŠIL

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague (Czechoslovakia)

SUMMARY

Mixtures of stabilizers, consisting of an antioxidant, light-absorber and synergist, designed to protect isotactic polypropylene against atmospheric ageing, were analysed by means of gel permeation chromatography. An acetone extract of the polymer was chromatographed on styrene-divinylbenzene gel having a molecular weight exclusion limit of 1000; the eluent was tetrahydrofuran. The values of the relative zone velocity, R , of some important stabilizers are listed and examples of quantitative analyses are discussed.

INTRODUCTION

Polyolefins are subject to thermo-oxidative and/or photo-oxidative degradation, and cannot be used in practical applications unless they are protected by means of efficient stabilizers. Isotactic polypropylene is especially sensitive to atmospheric oxygen. As a protection against ageing, mixtures of stabilizers can be used that consist of non-volatile and non-staining antioxidants, efficient light-absorbers and a synergist. The practical applicability of a polymer is determined by the proportions and the characters of the individual components of the mixture of stabilizers; it is therefore necessary to know its composition. The analytical procedures used involve chromatographic methods (paper, thin-layer and gas-liquid chromatography) mainly for the qualitative estimation of components¹⁻¹⁷. Modifications of some of these procedures are suitable also for quantitative determinations: thin-layer and column chromatography are used almost exclusively to separate individual components and the quantitative determination is performed afterwards by spectral^{1,7,10} or polarographic methods^{18,19}. To analyse mixtures of technical antioxidants, we used gel permeation chromatography (GPC)²⁰ and determined directly the contents of individual components.

TABLE I

GEL-CHROMATOGRAPHIC BEHAVIOUR OF SELECTED STABILIZERS (ANTIOXIDANTS AND SYNERGISTS) FOR ISOTACTIC POLYPROPYLENE

 $V_0 = 83.5$ counts.

Trade name	Composition	Mol. wt.	V_e (counts)	R
AO-4K	2,6-Di- <i>tert.</i> -butyl-4-methylphenol	220	129.8	0.643
Irganox 1076	Octadecyl 3-(3,5-di- <i>tert.</i> -butyl-4-hydroxyphenyl)propionate	530	100.8	0.828
AO 2246	2,2'-Methylenebis-(4-methyl-6- <i>tert.</i> -butylphenol)	340	116.5	0.717
AO 425	2,2'-Methylenebis-(4-ethyl-6- <i>tert.</i> -butylphenol)	368	113.7	0.734
Santowhite powder	4,4'-Butylidenebis-(3-methyl-6- <i>tert.</i> -butylphenol)	382	109.0	0.766
TBD	4,4'-Isopropylidenebis-(2- <i>tert.</i> -butylphenol)	340	109.0	0.766
TOD	4,4'-Isopropylidenebis-(2- <i>tert.</i> -octylphenol)	452	104.2	0.801
Santonox R	4,4'-Thiobis-(3-methyl-6- <i>tert.</i> -butylphenol)	358	111.9	0.746
Topanol CA	1,1,3-Tris-(5- <i>tert.</i> -butyl-4-hydroxy-2-methylphenyl)butane	544	100.8	0.828
Ionox 330	1,3,5-Trimethyl-2,4,6-tris-(3,5-di- <i>tert.</i> -butyl-4-hydroxybenzyl)benzene	756	98.9	0.844
Irganox 1010	Tetrakis [methylene 3-(3',5'-di- <i>tert.</i> -butyl-4'-hydroxyphenyl)propionate] methane	1176	88.9	0.939
DLT	Didodecyl 3,3'-thiodipropionate	336	102.8	0.812

TABLE II

GEL-CHROMATOGRAPHIC BEHAVIOUR OF SELECTED STABILIZERS (LIGHT ABSORBERS) FOR ISOTACTIC POLYPROPYLENE

 $V_0 = 83.5$ counts.

Trade name	Composition	Mol. wt.	V_e (counts)	R
—	<i>p</i> - <i>tert.</i> -Octylphenyl salicylate	326	128.6	0.649
—	α -Naphthyl salicylate	264	136.3	0.613
Uvinul N-539	2-Ethylhexyl β,β' -diphenyl- α -cyanoacrylate	347	120.5	0.693
Dastib 242	2-Hydroxy-4-(2-ethylhexyloxy)-benzophenone	252	123.4	0.677
Uvinul 400	2,4-Dihydroxybenzophenone	214	134.1	0.623
Cyasorb UV 24	2,2'-Dihydroxy-4-methoxybenzophenone	244	135.0	0.619
Tinuvin 320	2-(2-Hydroxy-3,5-di- <i>tert.</i> -butylphenyl)benzotriazole	303	127.9	0.653
Tinuvin 326	2-(2-Hydroxy-3- <i>tert.</i> -butyl-5-methylphenyl)-5-chlorobenzotriazole	314	134.4	0.621
Tinuvin 327	2-(2-Hydroxy-3,5-di- <i>tert.</i> -butylphenyl)-5-chlorobenzotriazole	357	123.8	0.674

EXPERIMENTAL

Stabilizers

All compounds listed in Tables I and II and used for the chromatographic analysis are commercial products; none of them was purified before the analysis. The chemical composition of these compounds is given in Tables I and II. Manufacturers: American Cyanamid Co. (AO 425, AO 2246, Cyasorb UV 24), Chemical Works of J. Dimitrov (AO-4K, Dastib 242, DLT, TOD), Ciba-Geigy A.G. (Irganox 1010, Irganox 1076, Tinuvin 320, Tinuvin 326, Tinuvin 327), General Aniline (Uvinul 400, Uvinul N-539), Imperial Chemical Industries Ltd. (Topanol CA), Institute of Macromolecular Chemistry, ČSAV (TBD), Monsanto Chemical Co. (Santonox R, Santowhite Powder) and Shell Chemical Co. (Ionox 330).

Preparation of samples of isotactic polypropylene

Mixtures were prepared from non-stabilized powdered isotactic polypropylene (CHISSO 5078) by mixing it with stabilizers in a Brabender plastograph (mixing time 5 min at 190° in a nitrogen atmosphere). The prepared mixtures were pressed into films at 200° for 10 min at a pressure of 200 atm/cm².

Extraction of samples of stabilized polypropylene

Stabilized polypropylene was mechanically disintegrated and extracted in a Soxhlet apparatus under a nitrogen atmosphere at a temperature near the boiling point of the extraction agent used. The apparatus was protected against daylight by using aluminium foil. Extraction times were 24 h for benzene and *n*-heptane and 8 h for acetone. The solvent used was evaporated in a rotating vacuum evaporator and the solid extract obtained was weighed and chromatographed.

Gel permeation chromatography

The room-temperature apparatus of our own construction²⁰ was used for the determination of the components in the extract. The gel chromatographic material S-GEL-832 (ÚMCH, ČSAV, Czechoslovakia) was packed into nine stainless-steel columns (1.2 m × 8 mm) connected in series. The pressure drop in the complete column system at a flow-rate of 35 ml/h during the analysis was about 10 atm. The last column was connected to a flow differential refractometer (Waters Associates, Model R-403), which was connected in series with a flow UV spectrometer (Development Workshops, ČSAV, Prague). Both detectors were connected to recorders which also simultaneously recorded the volume of eluate.

The residues obtained after the extraction of polymer were dissolved in tetrahydrofuran (THF) taken directly from the solvent tank of the chromatographic apparatus. Solutions (2–3%) of samples in THF were injected in volumes of 0.4–0.5 ml with an accuracy ±0.01 ml into the apparatus. The qualitative results (Tables I and II) were compared with those of thin-layer chromatographic (TLC) analysis (Table III). The contents of individual components were determined by measuring the heights of the corresponding peaks and by using the calibration curves for particular standard stabilizers.

TABLE III

 R_F VALUES OF STABILIZERS (TLC, SILUFOL UV₂₅₄) S_1 = Diisopropyl ether-*n*-heptane (1:1); S_2 = benzene-*n*-hexane (1:1).

Stabilizer	R_F	
	S_1	S_2
Topanol CA	0.29	0.0
Irganox 1076	0.72	0.31
Irganox 1010	0.38	0.0
Ionox 330	0.68	0.60
Santowhite powder	0.42	0.02
AO 425	0.60	0.34
AO 2246	0.58	0.32
Dastib 242	0.65	0.31
Tinuvin 326	0.75	0.72
Tinuvin 327	0.77	0.75
Tinuvin 328	0.72	0.72
Stabilizer DLT	0.52	0.03

RESULTS

In this paper, the results obtained by using the GPC method to determine the composition of stabilizers in the isotactic polypropylene CHISSO 5078 are given. The use of a suitable gel is a necessary condition for the identification and quantitative determination of components of a mixture of low-molecular-weight stabilizers in polymers.

Usually, the molecular weights of the components that form the stabilizing system of polypropylene do not exceed 800. Therefore the separations were performed on a gel having optimal resolution properties in this range. The molecular weight exclusion limit of the material used was 1000.

THF was selected as the eluent, because the gel swells excellently in this solvent and the solubility of all the components analysed is high. Its low absorbance of UV light at *ca.* 250 nm is also of advantage. This enables a common flow UV spectrometer to be used for both the qualitative and quantitative determinations of compounds that contain conjugated double bonds. The low refractive index of THF makes it suitable for use with a flow refractometric detector. By means of GPC it is possible to attain, at sufficiently high separation efficiency, the necessary resolution of almost all the individual components, even in the case of very complicated mixtures.

The suitability of the method was checked by analysing a large series of technical-grade light-absorbers, antioxidants and analogous model compounds. The relations between the chromatographic behaviour and the structures of the individual compounds will be discussed elsewhere. In this paper, values are given of elution volumes, V_e , and of relative zone velocities, R , for stabilizers that are used in practice at the present time in the polypropylene industry. Trade names and chemical compositions of typical compounds are listed. It is evident that GPC is suitable for the qualitative resolution of most antioxidants (Table I) as well as light-absorbers (Table II). From the results, it can be stated that almost all the antioxidants under study, as well as the commercial light-absorbers, are of extremely high purity. For the

initial qualitative determination of the components of the mixture of stabilizers we used TLC (with Silufol UV₂₅₄ silica-gel foils) in those cases where the V_e values of particular antioxidants or light-absorbers were too close together and did not sufficiently characterize the stabilizers. The results of the TLC analyses are given in Table III. Using proper standards, the method allows most individual compounds available as stabilizers for isotactic polypropylene to be distinguished.

The flow differential refractometer was used for detection in all analyses of stabilizer mixtures by GPC. The calibration proved that the dependence of the height of the chromatographic peaks on concentration is strictly linear within the concentration range that is important for the analysis of stabilizers. This enabled us to follow quantitatively the contents of the individual components in the complicated mixtures.

There were some difficulties in attempting to determine the contents of the synergist DLT (didodecyl 3,3'-thiodipropionate) which is almost always present in industrial mixtures together with some important antioxidants. Even if a "tailor-made" gel was used, the V_e values of DLT (synergist) and of Topanol CA and Irganox 1076 (antioxidants), representing the most unfavourable case, were too close (Table I). The quantitative determination of components by refractometric detection was impossible in this particular case. We therefore took advantage of differences between the chemical composition of DLT, which is an aliphatic compound, and of antioxidants which are of aromatic character. The convenient detection system was obtained by

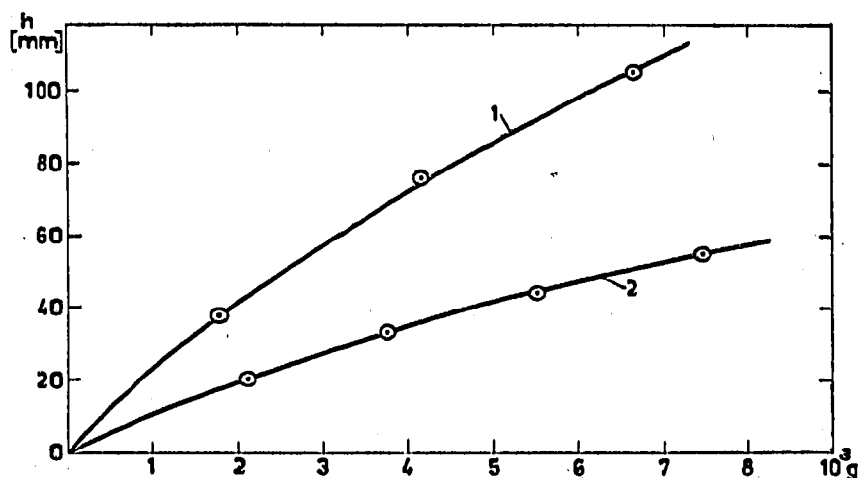


Fig. 1. Calibration curve for GPC Determination of Topanol CA (1) and Irganox 1076 (2) by using UV flow detector. h = Height of chromatographic peak, mm.

combining the flow differential refractometer and the flow UV detector in series. Each of the detectors was connected to its own recorder. Examples of UV calibrations of two antioxidants are given in Fig. 1, the heights of the peaks being plotted against concentration. The combination of both detectors made possible the determination of all components of the analysed mixture in a single chromatographic run.

We have chosen three typical examples to demonstrate the practical applicability of GPC to the analysis of stabilizers in polypropylene: The mixtures contained a non-volatile antioxidant [octadecyl-3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl) propionate (Irganox 1076) or 1,1,3-tris-(5-*tert.*-butyl-4-hydroxy-2-methylphenyl)butane (Topanol CA)], a light-absorber [2-(3,5-di-*tert.*-butyl-2-hydroxyphenyl)-5-chloro-

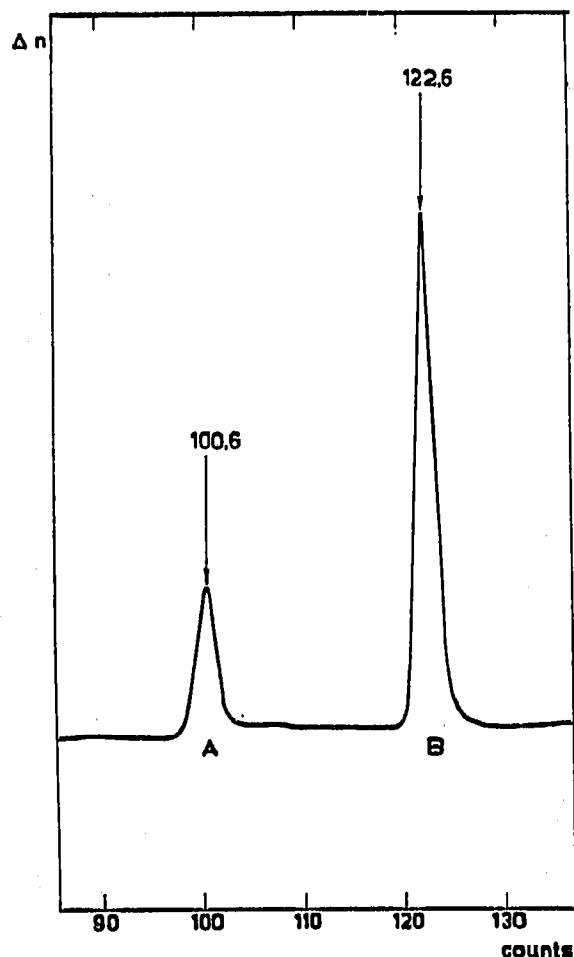
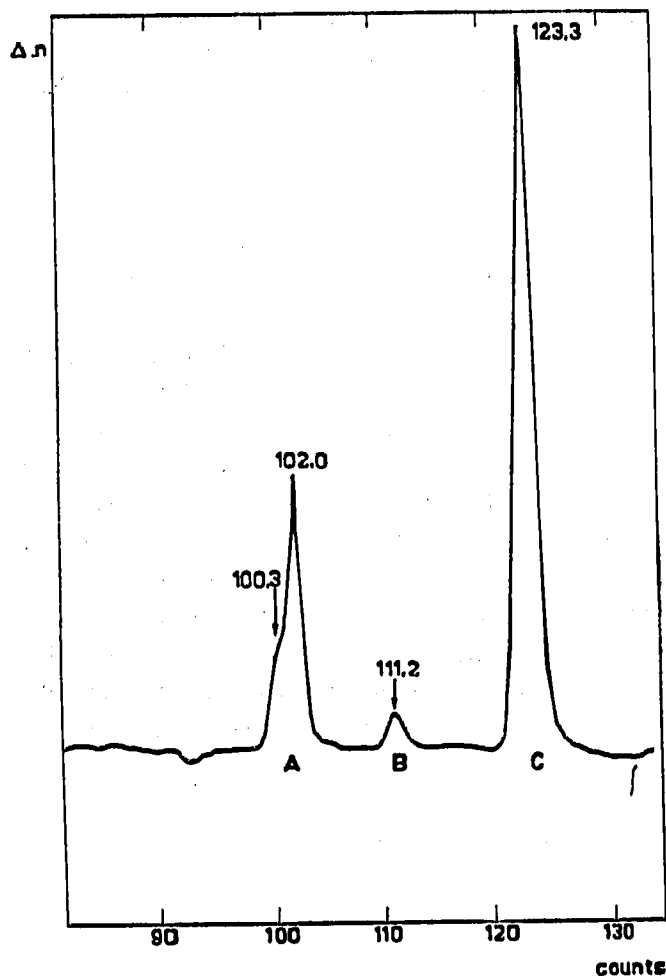


Fig. 2. Chromatogram of mixture of stabilizers No. 1 (Table IV). A = Topanol CA and stabilizer DLT; B = 2,4-bis-(2-ethylhexyloxy)benzophenone; C = Dastib 242.

Fig. 3. Chromatogram of mixture of stabilizers No. 2 (Table IV). A = Topanol CA and stabilizer DLT; B = Tinuvin 327.

benzotriazole (Tinuvin 327) or 2-hydroxy-4-(2-ethylhexyloxy)benzophenone (Dastib 242)] and a synergist [didodecyl 3,3'-thiodipropionate (Stabilizer DLT)]. Typical chromatograms of three-component mixtures of these stabilizers are given in Figs. 2-4.

Complete resolution and thus the quantitative determination of the stabilizers—with exception of DLT—was obtained. The chromatogram recorded by means of flow UV detector provided the concentration data of the aromatic antioxidants (Topanol CA and Irganox 1076). The amount of DLT could then be calculated as the difference from 100%. The fact that the amounts of DLT, Topanol CA and/or Irganox 1076 in THF solution are almost identical is rather fortuitous. The amounts of other common important antioxidants (for example, AO-425, Ionox 330 or Irganox 1010) were quantitatively recorded by the flow refractometer only (Table I).

The mixture of stabilizers must be extracted from the polymer before the analysis. At the start of the experiments, we measured the solubilities of the series of stabilizers under study in solvents that are suitable for the extraction of polyolefins.

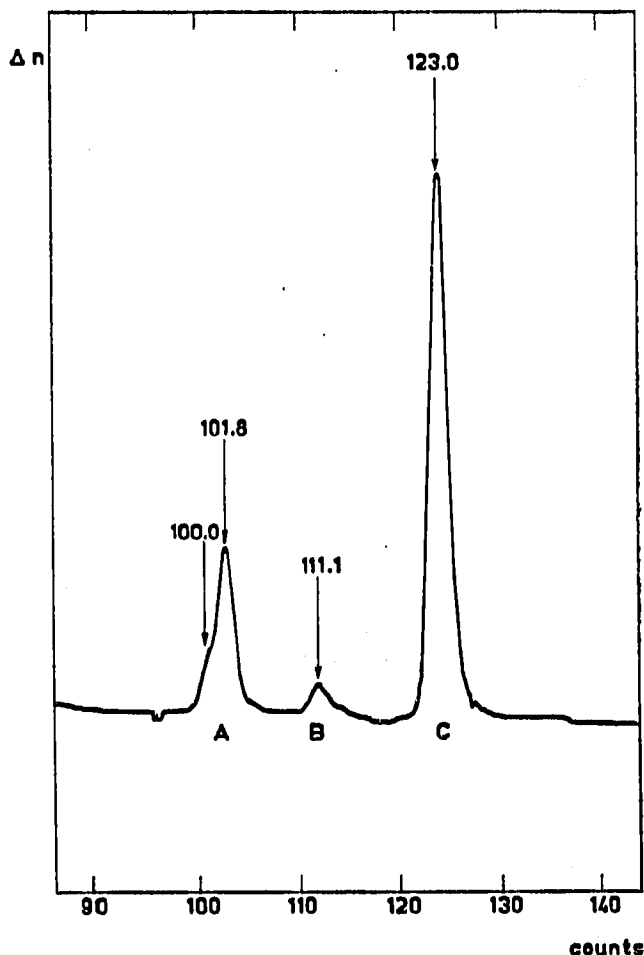


Fig. 4. Chromatogram of mixture of stabilizers No. 3 (Table IV). A = Irganox 1076 and stabilizer DLT; B = 2,4-bis-(2-ethylhexyloxy)benzophenone; C = Dastib 242.

It was found that in the case of hydrocarbon solvents, benzene or toluene was preferable to *n*-hexane or *n*-heptane since the aliphatic hydrocarbons do not dissolve sufficiently some components of the mixture of stabilizers. However, the hydrocarbon solvents possess a common disadvantage: they dissolve in the course of extraction about 3% of the oligomers present in the isotactic polypropylene CHISSO 5078.

These components are insoluble in the eluent (THF). For GPC analysis at room temperature, it is necessary to prepare a homogeneous solution of the extracted mixture having a concentration of 2–3%. Chlorobenzene might be used as a possible solvent for such an extract. The presence of oligomers in the analysed sample of polypropylene requires, however, a special calibration to enable the quantitative evaluation of the chromatogram to be carried out. In order to eliminate the extraction of oligomers together with the stabilizers, we used acetone. After the evaporation of the acetone, the extracts were completely dissolved in tetrahydrofuran and thus prepared for the direct analysis.

It should be noted that it is usually necessary to protect the extracted polymer, as well as the extract, against irradiation, and to perform the extraction under an inert atmosphere. This technique protects the sensitive components of the stabilizing system against chemical changes.

TABLE IV

ANALYSIS OF MIXTURES OF STABILIZERS BY GPC

Mixture No.	Components	Composition (%)	
		Theoretical	Found
1	Topanol CA	8.3	7.1
	Dastib 242	58.4	61.8
	DLT	33.3	31.1
2	Topanol CA	8.3	8.7
	Tinuvin 327	58.4	57.0
	DLT	33.3	34.3
3	Irganox 1076	8.3	8.4
	Dastib 242	58.4	55.2
	DLT	33.3	36.4

We determined the high reproducibility of GPC on styrene-divinylbenzene gel in analyses of individual stabilizers performed over longer periods of time²⁰. The results of the quantitative determination of components of typical mixtures of stabilizers are given in Table IV. These results confirm the suitability of GPC for the analysis of stabilizers in isotactic non-aged polypropylene.

REFERENCES

- 1 J. POSPÍŠIL, *Antioxidanty*, Academia Publishing House ČSAV, Prague, 1968, Ch. V.
- 2 V. KAPIŠINSKÁ AND M. KARVAŠ, *Chem. Prům.*, 21 (1971) 129.
- 3 F. R. CROMPTON, *Eur. Polym. J.*, 4 (1968) 473.
- 4 R. F. VAN DER HEIDE, *J. Chromatogr.*, 24 (1966) 239.
- 5 R. S. DOBIES, *J. Chromatogr.*, 40 (1969) 110.
- 6 J. G. KREINER AND W. C. WARNER, *J. Chromatogr.*, 44 (1969) 315.
- 7 J. SOUČEK, J. VAŠÁTKOVÁ AND I. ČÁDERSKÝ, *Chem. Prům.*, 16 (1966) 348.
- 8 H. AULER, *Identification of Antioxidants, Antiozonants and Accelerators by Means of TLC*, ETDC-Aachen, Material Research and Development, 1967.
- 9 H. S. KNIGHT AND H. SIEGEL, *Anal. Chem.*, 38 (1966) 1221.
- 10 J. PÁČ AND J. SEDLÁŘ, *Prepr. IVth French-Czechoslovak Meeting on Ageing of Polymers, Smolenice, 1970*.
- 11 R. E. LONG AND G. CH. GUVERNATOR, *Anal. Chem.*, 39 (1967) 1493.
- 12 A. FIORENZA, G. BONOMI AND A. SAREDI, *Rubber Chem. Technol.*, 41 (1968) 630.
- 13 V. KAPIŠINSKÁ, *Chem. Prům.*, 18 (1968) 265.
- 14 V. KAPIŠINSKÁ AND J. ŠMÍD, *Plast. Hmoty Kauč.*, 7 (1970) 144.
- 15 V. KAPIŠINSKÁ, V. KOSLJAR, E. Kardoš AND I. ORLÍK, *Plast. Hmoty Kauč.*, 6 (1969) 359.
- 16 V. KAPIŠINSKÁ AND V. KOSLJAR, *Plast. Hmoty Kauč.*, 6 (1969) 338.
- 17 J. KOREŇ, K. ONDREJMIŠKA AND A. BINKOVÁ, *Chem. Vldkna*, 18 (1968) 1.
- 18 K. FRANZKE, *Fette, Seifen, Anstrichm.*, 70 (1968) 472.
- 19 L. I. ZJUZINA, S. YA. CHAJKIN AND A. G. GOLDENBERG, *Plast. Massy*, 7 (1970) 66.
- 20 J. ČOUPEK, J. KAHOVEC, M. KŘIVÁKOVÁ AND J. POSPÍŠIL, *Angew. Makromol. Chem.*, 15 (1971) 137.

J. Chromatogr., 65 (1972) 279-286