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PYROLYSIS–GAS CHROMATOGRAPHY OF SOME CROSSLINKED COPOLYMERS OF STYRENE

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Abstract—The thermal degradation of copolymers of styrene, ethylstyrene and divinylbenzene with acrylonitrile and other acrylic monomers has been studied by pyrolysis–gas chromatography at 420, 570 and 790°. The thermal degradation products were identified and determined at 570°. The thermal degradation of some chloromethylated copolymers with the same composition was also followed. It has been ascertained that the chloromethylated copolymers show characteristic behaviour in thermal degradation. This is explained by modification of the degradation mechanism of the chloromethylated copolymers with respect to the development of crosslinking processes.

INTRODUCTION

One of the most useful applications of pyrolysis–gas chromatography is evaluation of the composition and the thermal degradation mechanism of binary copolymers; some styrene copolymers have been analysed on this way, viz styrene-acrylonitrile [1, 2] styrene-divinylbenzene [3, 4] styrene-methylmethacrylate [5–7], styrene-ethylacrylate [8] and styrene-methylacrylate [9]. Also, some information on the pyrolysis of methylmethacrylate- (*m*-, *p*-)divinylbenzene copolymers has been reported [10]. Analysis of copolymers of more than two comonomers is difficult, especially because of the great number of products evolved during degradation, so that there can be overlapping or superposition of some chromatographic peaks. Nevertheless, there are papers on ternary [11, 12] and quaternary [13] copolymers.

The present paper deals with the study by pyrolysis–gas chromatography of the thermal degradation of some crosslinked ternary and quaternary copolymers of styrene (the main component) with divinylbenzene and ethylstyrene, respectively, and acrylonitrile or other acrylic comonomers such as methyl methacrylate, n-butyl methacrylate, ethyl methacrylate and 2-ethylhexyl acrylate. The thermal behaviour of some chloromethylated copolymers of the same composition was also examined.

EXPERIMENTAL

The copolymers, with some characteristics concerning composition and polymerization conditions, are shown in Table 1.

The macroporous crosslinked copolymers listed in Table 1 were obtained by copolymerization in suspension [14], using respectively polystyrene ($\bar{M}_w = 75{,}000$), with pet. ether (b.p. 100–125°) or toluene as an inert medium.

The content of comonomers in the ternary copolymers was assumed to be equal to the initial monomer amount [15]; the acrylonitrile content was evaluated from the nitrogen content, obtained by elemental analysis of the copolymers [16].

Chloromethylation of the copolymers was carried out with monochloromethylether in the presence of anhydrous $ZnCl_2$ [17]. The chlorine contents of the chloromethylated copolymers were determined by Schöniger's method [18].

All polymer samples (0.40 mg) were pyrolysed in argon as carrier gas at three temperatures, viz 420, 570 and 790°, using a filament type pyrolysis unit described elsewhere [19]. Analysis of the pyrolysis products was carried out with a Siemens L-400 gas chromatograph provided with a flame ionization detector using the following operational conditions: chromatographic column (2 m × 3 mm i.d.) was packed with Chromosorb W (80–100 mesh) coated with 15% silicone SE-52; column temperature was first programmed from 60 to 180° at 7°/min and then operated isothermally at 180°; argon flow rate of 18.0 ml/min. Hydrogen chloride, evolved during the decomposition of chloromethylated copolymers, was adsorbed on a preliminary column with NaOH coated on asbestos to prevent deterioration of the supporting material of the chromatographic column.

As the sample size and pyrolysis time are important factors influencing the reproducibility of the results obtained by pyrolysis–gas chromatography, the working conditions were first established. The observed proportionality between the areas of the styrene and methyl methacrylate peaks for samples up to 0.5 mg of copolymer 3 (Fig. 1) suggests no influence of sample size. Therefore, we used samples of 0.4 mg in all experiments.

The influence of pyrolysis time, dependent on the pyrolysis temperature, is illustrated in Fig. 2, suggesting that at 420° the degradation is still not complete; at temperatures above 570°, additional decomposition of the main pyrolysis products (styrene and methyl methacrylate) may occur. For these reasons, a pyrolysis time of 30 sec at 570° was selected for routine analysis; at higher temperatures, the pyrolysis time was around 15 sec.

RESULTS AND DISCUSSION

Pyrolysis–gas chromatography shows essential differences between the original and chloromethylated copolymers (Figs 3 and 4).

The degradation products of the copolymers and the chloromethylated copolymers (pyrolysis temperature 570°) are presented in Tables 2 and 3.

Identification of the pyrolysis products was carried out by using the relative retention times of various reference substances and taking into consideration the

Table 1. Some characteristics of the macroporous styrene copolymers studied by pyrolysis–gas chromatography

	Chemical composition (%)				Inert medium	
Sample	Styrene	Ethylstyrene	Divinylbenzene	Chlorine	*Concentration (%)	Type
1	70.55	11.45	18.00	—	60.00	pet. ether
2	70.55	11.45	18.00	14.99	60.00	pet. ether
	Methylmethacrylate—20.00%					
3	50.55	11.45	18.00	—	60.00	pet. ether
4	50.55	11.45	18.00	12.89	60.00	pet. ether
	Ethylmethacrylate—5.00%					
5	81.50	5.500	8.00	—	25.00	polystyrene
6	65.52	11.48	18.00	—	60.00	pet. ether
7	49.35	18.65	27.00	—	60.00	toluene
	n-*Butyl-methacrylate—20.00%*					
8	49.55	12.45	18.00	—	60.00	pet. ether
9	49.55	12.45	18.00	13.26	60.00	pet. ether
	Acrylonitrile—10.34%					
10	76.56	5.10	8.00	—	25.00	polystyrene
11	46.53	11.47	18.00	—	60.00	pet. ether
12	46.53	11.47	18.00	6.22	60.00	pet. ether
	2-Ethyl-hexyl-acrylate—5.00%					
13	65.52	11.48	18.00	—	60.00	pet. ether

* Concentration of the inert medium is given in volume/volume for pet. ether and toluene, and weight/weight for polystyrene.

results of Blasius *et al.* [20] and Oehme *et al.* [21] on the thermal degradation products of styrene-divinylbenzene copolymers.

The measured values show that the nature and the proportion of the products depend on the nature of the pyrolysed copolymers. All analysed copolymers evolve main common decomposition products such as styrene, ethylstyrene and divinylbenzene but there is a possibility of differentiating the quaternary copolymers by the products characteristic of the fourth comonomer. Thus, the copolymers with methacrylate and *n*-butyl methacrylate evolve respectively methyl methacrylate and *n*-butyl methacrylate. Specific to the copolymers with *n*-butyl methacrylate are butene and butyl alcohol, the latter being evolved in smaller amounts.

The important differences between the quantitative and qualitative composition of the decomposition products are characteristic for the styrene/ethylstyrene/divinylbenzene/2-ethylhexyl acrylate copolymers, while the content of the fourth component, i.e. 2-ethylhexyl acrylate, is very small (5%). However these copolymers may be identified either by hexene and/or by 2-ethylhexyl acrylate.

Plotting the chromatographic peak areas of the main pyrolysis products of the copolymers with ethyl methacrylate (samples 5, 6 and 7) against the copolymer composition, straight lines were obtained

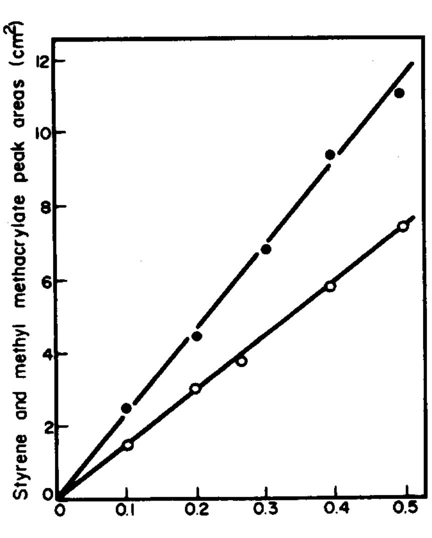

Fig. 1. The influence of sample size on the styrene and methyl methacrylate chromatographic peak areas (copolymer sample 3). (●) Benzene: (O) methyl methacrylate.

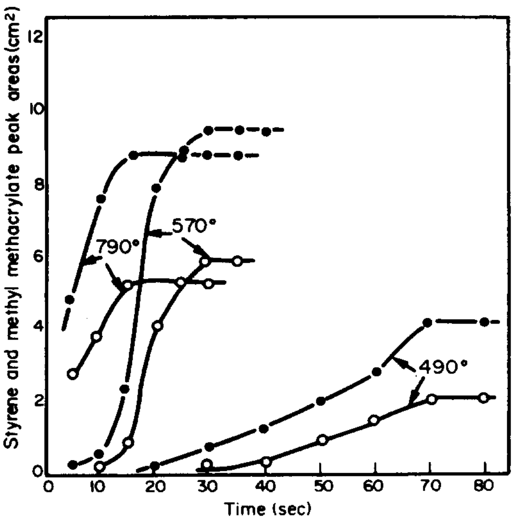

Fig. 2. The influence of pyrolysis time on the styrene and methyl methacrylate chromatographic peak areas (copolymer sample 3). (●) benzene: (O) methyl methacrylate.

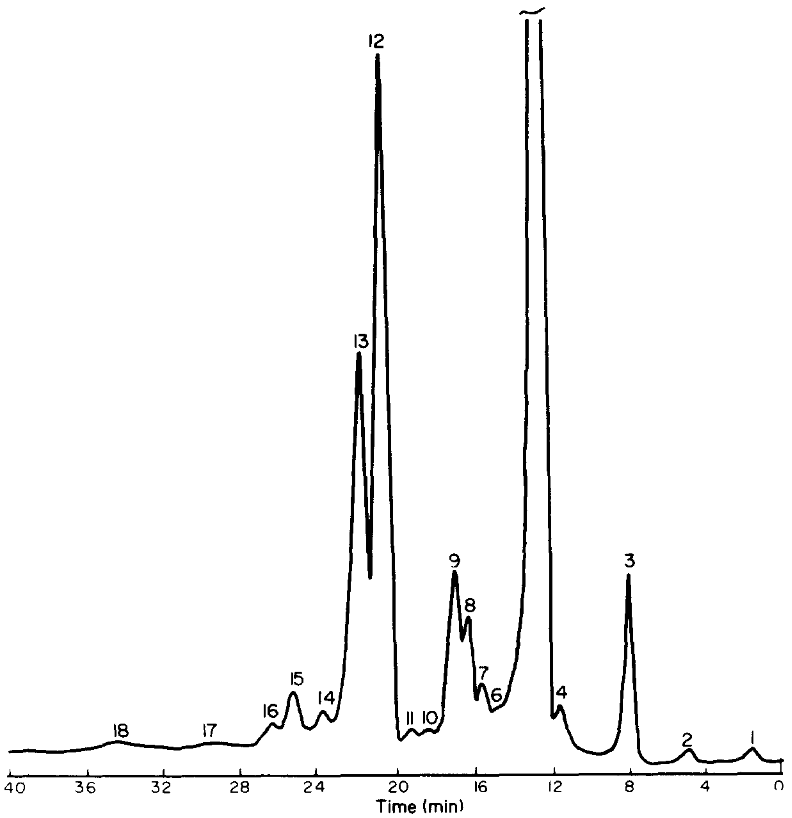

Fig. 3. Pyrogram of the styrene ethylstyrene divinylbenzene ternary copolymer at 570° (copolymer sample 1). 1—volatile hydrocarbons C_1—C_3; 2—benzene; 3—toluene; 4—ethylbenzene; 5—styrene; 6—isopropylbenzene; 7—α-methylstyrene; 8—ethyltoluene; 9—vinyltoluene; 10—unidentified; 11—butylbenzene; 12—ethylstyrene; 13—divinylbenzene; 14–18—compounds with high boiling points (b.p. > 180°).

(Fig. 5); they may be used to determine the composition of these copolymers.

The chloromethylated copolymers show, together with hydrochloric acid (not indicated by gas chromatography due to the used detection system, but found by supplementary analysis, viz passing the evolved gases from pyrolysis into $AgNO_3$ solution; also, thermogravimetric analysis showed two degradation

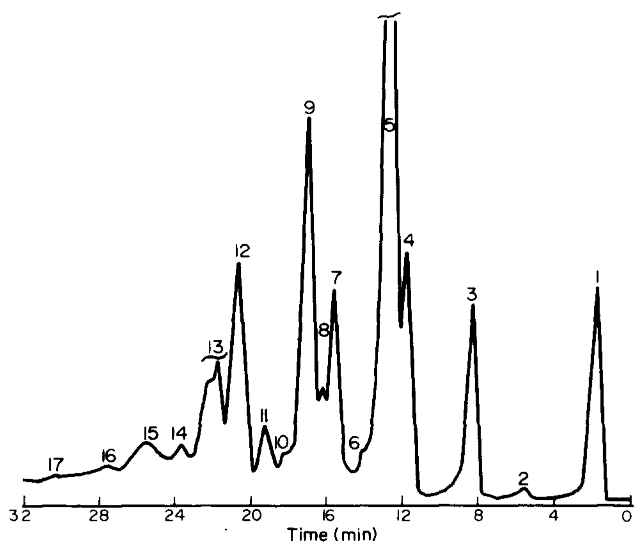

Fig. 4. Pyrogram of the chloromethylated styrene ethylstyrene divinylbenzene ternary copolymer at 570° (copolymer sample 2). 1—volatile hydrocarbons; C_1—C_3 + CH_3Cl; 2—benzene; 3—toluene; 4—ethylbenzene; 5—styrene; 6—isopropylbenzene; 7—α-methylstyrene; 8—ethyltoluene; 9—vinyltoluene + benzyl chloride; 10—unidentified; 11—butylbenzene; 12—ethylstyrene; 13—divinylbenzene; 14–17—compounds with high boiling points (b.p. > 180°).

Table 2. Decomposition products of the original copolymers pyrolysed at 570°

	Sample Content %					
Compound	1	3	6	8	11	13
Hydrocarbons C_1-C_3	0.32	0.84	3.87	0.63	0.78	0.54
Butene	—	—	—	16.21	—	—
Hexene	—	—	—	—	—	0.13
Methanol	—	0.08	—	0.12	—	—
Acrylonitrile	—	—	—	—	2.80	—
Benzene	1.28	0.29	0.86	0.54	0.24	0.81
Methyl methacrylate	—	—	20.78	—	—	—
Ethyl acrylate	—	3.76	Trace	—	—	4.34
Toluene	6.34	1.59	2.57	2.10	4.05	8.08
Ethyl methacrylate	—	—	0.41	—	—	—
Butanol	—	—	—	0.11	—	—
Ethylbenzene	1.87	0.24	0.84	0.45	0.48	0.75
Styrene	42.91	39.56	43.96	33.67	43.75	34.73
Isopropylbenzene	Trace	0.12	0.08	0.06	Trace	
α-Methylstyrene	0.87	0.53	3.14	1.35	0.59	1.20
Butyl methacrylate	—	—	—	13.77	—	—
Ethyltoluene	3.17	0.90	3.08	1.20	2.56	1.37
Vinyltoluene	3.21	3.72	3.36	1.84	4.02	5.08
Butylbenzene	0.30	0.25	0.26	0.19	0.49	0.31
Ethylstyrene	20.71	19.10	17.21	16.06	20.33	19.43
Divinylbenzene	11.91	10.63	12.06	8.23	12.34	15.10
2-Ethylhexyl acrylate	—	—	—	—	—	2.70
Compounds with high boiling points (> 180°)	6.88	3.38	4.0	3.06	6.44	4.20

steps, the first corresponding to evolved hydrochloric acid), two other chloro-compounds viz methyl chloride and benzyl chloride. Unfortunately, the chromatographic peaks for these compounds overlapped those for other compounds (peaks 1 and 8 in the chromatograms), thus they could not be quantitatively determined. The appearance of these chlorinated compounds explains the important increase of the peak

Table 3. Decomposition products of the chloromethylated copolymers pyrolysed at 570°

	Sample Content %			
Compound	2	4	9	12
Hydrocarbons C_1-C_3; Chloroform	9.1	9.27	8.89	4.44
Butene	—	—	27.68	—
Methanol	—	Trace	1.37	—
Acrylonitrile	—	—	—	6.79
Benzene	0.76	0.15	0.93	1.85
Methyl methacrylate	—	23.17	—	—
Ethyl acrylate	—	Trace	—	—
Toluene	7.45	3.27	4.89	5.35
Ethylbenzene	10.40	3.64	5.96	1.26
Styrene	32.71	25.85	14.36	37.43
Isopropylbenzene	0.07	Trace	0.11	Trace
α-Methylstyrene	8.82	5.50	4.12	4.54
Butyl methacrylate	—	—	8.69	—
Ethyltoluene	0.23	0.08	Trace	1.49
Vinyltoluene; benzyl chloride	9.89	8.31	5.85	5.71
Butylbenzene	5.0	2.88	1.74	0.80
Ethylstyrene	11.14	7.71	4.89	13.35
Divinylbenzene	1.64	5.53	4.18	8.21
Compounds with high boiling points (> 180°)	2.60	4.44	5.11	8.71

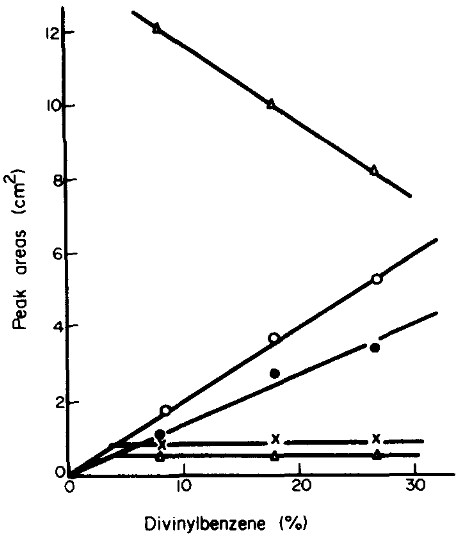

Fig. 5. The dependence of the chromatographic peak areas of styrene, ethylstyrene, divinylbenzene, toluene and ethyl methacrylate on the divinylbenzene content of the copolymers with ethylmethacrylate (copolymer samples 5–7). (△) styrene; (○) ethylstyrene; (●) divinylbenzene; (×) toluene and (▲) ethyl methacrylate.

areas 1 and 8 (Fig. 2) compared with the same peak areas in Fig. 1. The chloromethylated copolymers show an important decrease in the quantities of the main pyrolysis products i.e. styrene, divinylbenzene and ethylstyrene.

These results may be explained by a possible modification of the degradation mechanism of the chloromethylated copolymers, i.e. by assuming that some cross-linking occurs as a result of the primary elimination of hydrochloric acid especially from—CH_2Cl groups in the *para* position of the styrene ring. This cross-linking process during thermal degradation of chloromethylated copolymers explains also the apparent higher thermal stability suggested by the results shown in Fig. 6, where all the chromatographic peak areas of the pyrolysis products are presented for comparison.

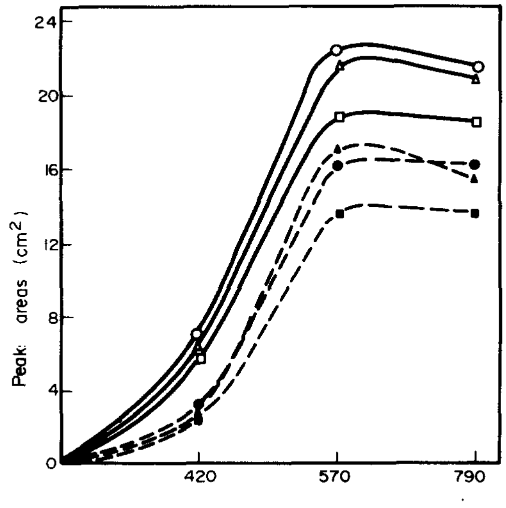

Fig. 6. The temperature dependence of the chromatographic peak areas of the pyrolysis products. (——) original copolymers; (· · · ·) chloromethylated copolymers. (○) sample 1; (△) sample 8; (□) sample 11; (●) sample 2; (▲) sample 9; (■) sample 12.

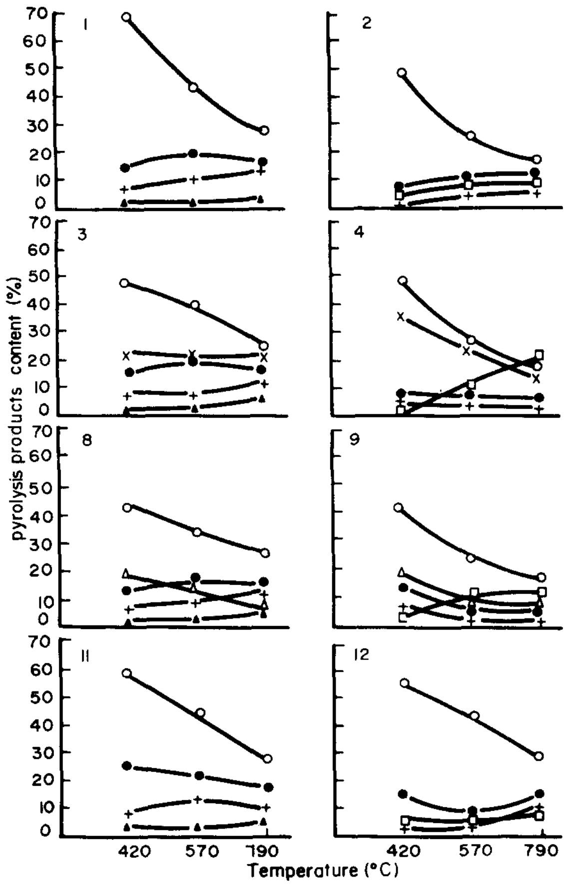

Fig. 7. The temperature dependence of the main pyrolysis products of the original and chloromethylated copolymers (samples 1–4, 8, 9 and 11). (○) styrene; (●) ethylstyrene; (×) methyl methacrylate; (△) *n*-butyl methacrylate; (+) divinylbenzene; (▲) volatile hydrocarbons C_1—C_3; (□) volatile hydrocarbons C_1—C_3 + $ClCH_3$.

The two sets of copolymers show also important differences concerning the degradation temperature dependency. (especially for the volatiles) which may be explained by the appearance of CH_3Cl in the products from chloromethylated copolymers (Fig. 7).

REFERENCES

1. D. Braun and R. Disselhoff, *Makromolek. Chem.* **23,** 103 (1972).
2. R. Vucović and V. Gnjatović, *J. Polym. Sci., A*-1 **8,** 139 (1970).
3. V. Svob and F. Flajsman, *Croat. chem. Acta* **42,** 417 (1970).
4. R. H. Wiley, G. DeVento and F. E. Martin, *J. Macromolek. Chem.* **1,** 137 (1966).
5. R. S. Lehrle and J. C. Robb, *J. gas Chromat.* **5,** 89 (1967).
6. K. V. Alekseeva, L. P. Khramova and L. S. Solomtina, *J. Chromat.* **77,** 61 (1973).
7. L. D. Turkova and B. G. Belenkii, *Vysokomelek. Soedin.* **12,** 467 (1970).
8. H. McCormick, *J. Chromat.* **40,** 1 (1969).

9. K. J. Bombaugh, C. E. Cook and B. H. Clampit, *Analyt. Chem.* **35,** 1834 (1963).
10. R. H. Wiley and F. E. Martin, *J. Macromolek. Sci. Chem.* **A1,** 635 (1967).
11. V. P. Alishoev, V. G. Berezkin, S. M. Lashova, G. A. Mirjabaev, G. N. Petrov, G. M. Tolstopyatov and E. M. Viktorova, *Vysokomolek. Soedin.* **13,** 2777 (1971).
12. D. F. Nelson, Y. L. Yee and P. L. Kirk, *Microchem. J.* **6,** 255 (1962).
13. J. K. Haken and D. M. K. Ho, *J. Chromat.* **126,** 239 (1976).
14. Ig. C. Poiescu, S. Drăgan, S. Maxim and M. Dima. *Revue roum. Chim.* **20,** 1311 (1975).
15. T. Alfray Jr and H. S. Pinner, *J. Polym. Sci.* **23,** 533 (1957).
16. T. S. Ma and G. Zuazaga, *Ind. Engng Chem. analyt. Edn* **14,** 280 (1942).
17. S. Maxim, Ig. C. Poinescu, S. Drăgan and M. Dima, *Revue roum. Chim.* **17,** 1437 (1972).
18. J. Hasslam, J. B. Hamilton and D. C. M. Squirell, *Analyst* **85,** 556 (1960).
19. C. N. Caşcaval, H. Oleinek, I. Zugrăvescu and I. A. Schneider, *Makromolek. Chem.* **169,** 129 (1973).
20. E. Blasius, J. B. Lohde and H. Häusler, *Z. analyt. Chem.* **264,** 278 (1973).
21. G. Oehme, H. Baudisch and H. Mix, *Makromolek. Chem.* **177,** 2657 (1976).