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FRACTIONATION OF END-LABELLED POLYSTYRENES BY SILICA GEL COLUMN CHROMATOGRAPHY

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SUMMARY

Column chromatography of bis-OH-end-labelled polystyrene on silica gel, using increasing amounts (0.01 to 2%) of methanol in chloroform, gave fractions of diffent molecular weight and narrower molecular weight distributions. HO-Polystyrene-OH of high molecular weight eluted before fractions of lower molecular weight. Similar fractionation was obtained with bis-4-(1′-pyrenyl)-butyrate esters of these polymers, but the individual fractions had larger $\bar{M}_w/\bar{M}_n$ values than in the chromatography of the OH-terminated polymers.

INTRODUCTION

A situation frequently encountered in polymer science is the need to fractionate synthetic polymers into samples of narrower polydispersity. Classically, the technique of fractional precipitation[1,2] has been used to precipitate selectively the higher-molecular-weight components of a polydisperse mixture through the proper choice of temperature and solvent–non-solvent combination. More recently gel-permeation techniques[2] have been found useful, either with free standing columns or by high-performance liquid chromatography (HPLC). Little emphasis has been placed on adsorption chromatography, although there have been some reports that low-molecular-weight polymers can be fractionated into the pure oligomers by HPLC on silica gel[4]. Adsorption chromatography has also been used in conjunction with HPLC techniques to measure the molecular weights of polymers[5].

In this report, we describe the application of thin-layer chromatography (TLC) to the analysis of end-labelled polystyrenes, and the extension of this technique to the fractionation of polymers by simple column chromatography on silica gel.

EXPERIMENTAL

OH-end-capped polystyrene (I)

The polymer samples were prepared by the initiation of styrene polymerization in tetrahydrofuran by naphthyl potassium at −60°C[5]. The carbanions at both ends

of the living polymer were quenched by reaction with ethylene oxide at $-70°C$ followed by a slow warm-up to room temperature. When the last traces of the rose color of the benzyl anion disappeared, the gel-like reaction mixture was treated with excess glacial acetic acid. This now fluid solution was added dropwise to a 10-fold excess of methanol to precipitate the polymer.

ROCH$_2$CH$_2$(CHCH$_2$)$_x$ (CH$_2$CH)$_y$ CH$_2$CH$_2$OR

R = H

I

R =

CH$_2$CH$_2$CH$_2$C—

II
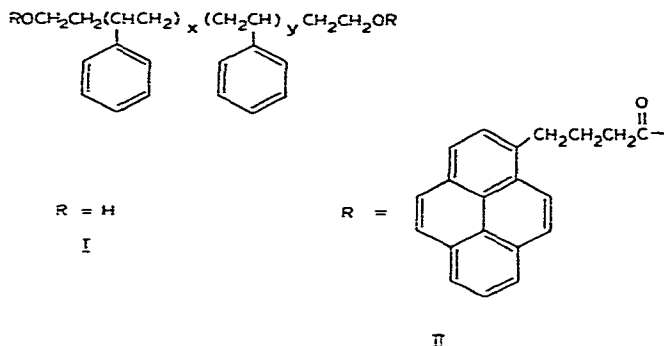
Pyrene end-capped polymer (II)

Pyrene groups were attached to both ends of the polymer by the reaction of typically 200 mg HO-polystyrene-OH with an excess (30 mg) of β-(1'-pyrenyl)butyroyl chloride in 5 ml toluene containing a slight excess (0.5 ml) of dry pyridine. This polymer was normally recovered by stirring briefly over small quantities of silica gel (100 mg) and activated charcoal (50 mg) followed by filtration and precipitation by dropwise addition into 50 ml of methanol.

In one experiment discussed in detail, 2.6 g of HO-polystyrene-OH ($\bar{M}_n$ 12,000, $\bar{M}_w/\bar{M}_n$ 1.78) was treated with 0.26 g β-(1'-pyrenyl)butyroyl chloride in 25 ml toluene containing 0.6 ml of pyridine. After stirring four days in the dark, 300 mg of activated charcoal was added and the mixture, after stirring 30 min, was poured onto the top of a 1-cm diameter column previously slurry packed with silica gel in benzene–cyclohexane (7:3, v/v). This chromatography, called Column II, will be described below.

Polymer characterization

Molecular weights of the polymer samples were obtained by gel permeation chromatography, using a Waters Model 6000 pump in combination with 10^4-, 10^3-, and 500-Å μStyragel columns. End group analysis by UV spectroscopy provided an independent measure of $\bar{M}_n$ for the pyrene-labelled material. For this analysis we used $\varepsilon_{345} = 3.83 \cdot 10^4 \ M^{-1} \ cm^{-1}$.

TLC plates were 0.25-mm thick silica gel plates from Analtech. These were 10 × 2.5 cm in size and contained a fluorescent binder. For column chromatography 70–200 mesh silica gel was obtained from Macherey, Nagel and Co. (MN Kieselgel 60). Silica gel of higher activity was ineffective in fractionating the polymers.

Solvents for TLC and column chromatography were ACS grade. Chloroform, however, was purified of added ethanol by distillation from P_2O_5. Fractions from column chromatography were concentrated to 1 to 2 ml on a rotary evaporator. Then the polymer was precipitated by adding this solution dropwise to 30 ml methanol. The solid polymer was collected by filtration and then dried *in vacuo* over P_2O_5.

RESULTS AND DISCUSSION

Thin-layer chromatography

TLC appeared to be a suitable technique for monitoring the extent of conversion of HO-polystyrene-OH to the corresponding bis-pyrenebutyryl ester. Based upon the detailed studies of Inagaki[7] and Otocka et al.[8] it was expected that suitable TLC conditions could be established for the separation of OH-terminated polymer from pyrene-terminated polymer. The initial studies, however, were frustrated by the tendency of the polymers to form streaks on the TLC plates. On recognizing that the origin of these streaks was the chain length sensitivity of R_F, it was attempted to take advantage of this phenomenon for fractionating the polymers.

Inagaki[7] has recently pointed out that three separate mechanisms contribute to the TLC separation of polymers, viz. adsorption, partitioning, and molecular sieving. We had hoped to take advantage of preferential adsorption of the OH-groups on the silica gel during TLC analysis of the reaction mixtures. Initially a solvent was sought to provide a significant migration on TLC for the bis-pyrenyl ester II. These polymers showed $R_F = 0$ with cyclohexane as the eluent, or with mixtures of cyclohexane and benzene containing 50 % (v/v) or less benzene. In pure benzene $R_F = 1$ was found. Cyclohexane–benzene (4:1) caused II to streak, suggesting that the R_F value might depend on molecular weight.

To the contrary, the OH-terminated polymer showed short streaks of low R_F in this mixture. Longer streaks with $R_F \leqslant 0.8$ were found for OH-terminated polystyrene of $\bar{M}_n = 25,000$ in both pure benzene and pure chloroform as eluents. In chloroform the extent of streaking was sensitive to $\bar{M}_n$, with higher-molecular-weight samples having larger R_F values. Another very attractive solvent mixture was cyclohexane–benzene (1:1) containing 1 % methanol. This was one of the few TLC solvents to separate, and hence to show the presence of, low-molecular-weight impurities in the pyrene-terminated polymers.

Column chromatography

One of the interesting features of the TLC experiments was that for the polymer samples of $\bar{M}_n$ 3000 to 50.000. the high-molecular-weight polymers seemed to have larger R_F values than the low-molecular-weight samples. This was true for both the OH-end capped polymers I and the pyrene-ester capped polymers II. This suggested that column chromatography on silica gel might be able to fractionate the polymers, with the high-molecular-weight material eluting first. Such a result would be somewhat surprising, since in HPLC of polystyrene lacking polar end groups, the lower-molecular-weight components normally elute before the higher ones[4,5].

Indeed, it was possible to fractionate up to 6 g of OH-terminated polystyrene, achieving polydispersities as low as 1.05 and more typically 1.09 to 1.16, and at the same time remove traces of polymer which did not contain two OH-groups. It also was possible to fractionate the pyrene-terminated polymer while quantitatively removing low-molecular-weight impurities introduced diving esterification.

While the general procedure for the column chromatography was straight-forward, the particular solvent necessary to elute a particular molecular weight was very sensitive to the activity of the silica gel, day-to-day changes in atmospheric humidity and (presumably) the moisture content of the various solvents used.

In a typical experiment, a column (35 × 5 cm) containing 280 g of silica gel was slurry packed using 400 ml chloroform distilled from P_2O_5. The column was allowed to stand over night, then charged with 2.8 g of OH-terminated polystyrene dissolved in a minimum amount (5 to 10 ml) of chloroform. The column was eluted with chloroform and then chloroform containing traces (0.01 % to 2 % methanol); 100 ml fractions were collected. The first fraction often contained naphthalene, an impurity from initiation of the polymer synthesis. High-molecular-weight polymer came off the column next, followed by polymers of continuously decreasing molecular weight. It should be noted that less than 100 % (typically about 80 %) of the total polymer was recovered, with the lost material being the highest-molecular-weight fraction. In general the polydispersity of fractions of $\bar{M}_n \geqslant 50,000$ was noticeably poorer than that for low-molecular-weight fractions and there was difficulty in getting the highest molecular weight (10^5) material to come off the column at all under these conditions. However, serious attempts to optimize conditions for these polymers have not been made. Data from one such chromatography of OH-terminated polystyrene of $\bar{M}_w/\bar{M}_n = 1.58$ are shown in Table I.

TABLE I

FRACTIONATION OF OH-TERMINATED POLYSTYRENE OF $M_n = 8000$, $\bar{M}_w/\bar{M}_n = 1.58$ BY SILICA GEL CHROMATOGRAPHY.

Chromatography of 2.8 g of OH-terminated polystyrene on 280 g of silica gel, packed in chloroform and eluted with 0.01 % to 2 % (v/v) methanol in chloroform.

Fraction*	Weight collected (mg)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
2	420	>20,000	—
3	370	17,500	1.11
5	180	14,500	1.10
6	130	13,400	1.10
8	160	12,400	1.05
12	150	8200	1.06
13	130	7500	1.08
14	200	5200	1.16
15	290	4700	1.23
16	180	4500	1.19
17	170	4700	1.20
18	100	4100	1.17

* 100-ml fractions.

Several further comments are in order. Reasonable fractionations could not be achieved if the silica gel were too active, (the Macherey, Nagel & Co. silica gel used is quite an inactive material). More annoying is that the amount of methanol necessary to induce elution and fractionation of the polymer varied from day to day, due, presumably, to the variation in atmospheric humidity mentioned earlier. A feeling for the procedure became necessary, —the technique remains more of an art than a science.

Several experiments were conducted to see if silica gel chromatography could

mass fractionate the pyrene-terminated polystyrene and also serve to separate any traces of remaining OH-terminated polymer. Since the pyrene end group readily photooxidizes, these columns were run rapidly in a darkened room partly illuminated with yellow fluorescent lights. These experiments were not as extensive as those with the OH-terminated polymer, as the results of the latter were more promising. One example studied in detail is reported below:

Pyrene-terminated polystyrene was synthesized from 2.6 g of HO-terminated polystyrene ($\bar{M}_n = 12{,}000$, $\bar{M}_w/\bar{M}_n = 1.78$), as described in the Experimental section. At the end of the reaction, after stirring the reaction mixture with a bit of charcoal, the entire product was poured on top of a silica gel column previously slurry packed in benzene–cyclohexane (7:3). Elution was begun at once. A substantial amount of high-molecular-weight material was eluted only slightly after the solvent front (Table II). No further material eluted until the solvent was changed to benzene–cyclohexane (3:1). Subsequent fractions contained 60 to 100 mg of polymer of decreasing molecular weight. The polydispersities obtained in these columns was significantly broader than that obtained by the chromatography of the OH-terminated polystyrene described in Table I.

TABLE II

FRACTIONATION OF PYRENE–(CH$_2$)$_3$–$\overset{\overset{\displaystyle O}{\|}}{C}$O–CH$_2$–CH$_2$–POLYSTYRENE–CH$_2$–$\overset{\overset{\displaystyle O}{\|}}{O}$C(CH$_2$)$_3$– PYRENE OF $\bar{M}_n = 12{,}000$, $\bar{M}_w/\bar{M}_n = 1.78$ BY SILICA GEL CHROMATOGRAPHY

Chromatography of *ca.* 2.8 g of polymer on 100 g silica gel, packed in benzene–cyclohexane (7:3, v/v). 100-ml fractions.

Fraction	Weight collected (mg)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
2–7	500	33,000	1.41
19–20*	60	22,200	1.37
21–22	140	20,800	1.26
23	100	20,600	1.31
24	100	17,400	1.29
25	80	15,400	1.26
26	90	13,800	1.34
27	100	13,100	1.22
28	70	12,400	1.23
29**	75	11,400	1.23
30	60	11,000	1.21
31	60	10,300	1.23
32	70	9700	1.21
33	75	9600	1.22
34	100	9400	1.27
35	80	9000	1.22
36	70	8900	1.25
37–39	150	8500	1.26
40–42	150	8000	1.31

* Eluent changed to benzene–cyclohexane (75:25, v/v).
** Eluent changed to benzene–cyclohexane (80:20, v/v).

Mechanism of the separation

Since both benzene–cyclohexane (1:1) and chloroform are good solvents for the polymer, partition is unlikely to play an important role in these separations as it would if the eluent were a solvent–non solvent–non-solvent mixture. Molecular sieving effects would contribute to the separations obtained but their overall importance was limited in that solvents of increasing solvent power were necessary to remove the polymers with shorter chains from the column.

The major source of the separations achieved is most likely the differential adsorption of the polar chain ends to the silica gel relative to the adsorption of the chain itself. In benzene, toluene and chloroform, chain adsorption is not significant, since by TLC an $R_F = 1$ was observed for polystyrene samples lacking OH-end groups. In this respect, traces of methanol added to the solvent compete with the polymer end groups for sites on the silica gel and induces chain migration. One of the interesting features of our observations was that if the silica gel were too active, separations could not be achieved at all. It seems that conditions necessary to induce polymer elution were too stringent to permit selective end-group adsorption.

NOTE ADDED IN PROOF

Two recent papers report the separation of end-functionalized polymers by column chromatography. HO-end-capped poly(methyl methacrylate) separations are presented by G. D. Andrews and A. Vatvars, *Macromolecules*, 14 (1981) 1605–1607. Carboxyl-end-capped polystyrene separations are discussed by P. Mansson, *J. Polym. Sci. Polym. Chem. Ed.*, 18 (1980) 1945.

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