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Preparative GPC in fundamental polymer synthesis

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Summary

A simple efficient preparative gel permeation chromatography assembly (prep GPC) has been built using largely commercially available components, (i.e., pump, columns, all glass solvent recirculating system) and its usefulness in fundamental polymer synthesis was demonstrated. The operating cost of prep GPC has been reduced and the safety much improved by the use of n-hexane as the mobile phase. Rapid one-recycle narrow fractionation (M_w/M_n = 1.1-1.2) and purification of relatively large quantities (up to 20 g/loading) of polyisobutylene (PIB) samples is described. Operating parameters and efficiency are illustrated by examples. By the use of this equipment sufficient quantities of narrow MWD polyhydrocarbons can be conveniently and rapidly obtained for meaningful structure/property research.

Introduction

The importance of the analytical aspect of GPC is well documented, however, little effort has been made to extend the use of this important technique for the fractionation of polymer samples on a preparative scale (1,2). The recent commercial availability of prep GPC equipment has prompted us to examine this novel capability in fundamental polymer synthesis. The use of prep GPC has not yet been described for the fractionation and purification of polyisobutylenes whose precise synthesis is of great interest to us. Specifically we wished to develop routine capability for the preparation of well-defined polyhydrocarbons with narrow molecular weight distributions (MWD) for subsequent structure/property characterization research.

One draw-back of prep GPC is the relatively large quantity of solvent required for operation. To alleviate this shortcoming we have designed a continuous solvent recirculating system which after the first charging of the assembly virtually eliminates the need for additional solvent. By the use of this recirculating system the operating cost of prep GPC has been reduced to a fraction of that of conventional once through-redistill cycles, and thus brought preparative capability into cost conscious smaller or academic laboratories.

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The aim of this communication is to describe a simple prep GPC assembled from largely commercially available components for the narrow fractionation of hydrocarbon polymers, in particular polyisobutylenes (PIB) of $\bar{M}_n < 10^4$. The assembly comprises a pump, two preparative columns and a novel "home grown" all-glass solvent recirculating system. The capability of the equipment is illustrated by fractionation data on select PIB samples.

Experimental

Materials

Two PIB samples have been prepared by living carbocationic polymerization technique (3) and their $\bar{M}_n$s were determined by analytical GPC (Waters Analytical GPC, Model 6000; equipped with dual detectors: a Differential Refractometer R-401, and a UV Absorbance Detector Model 440; operating with five Ultrastyragel columns of 100, 500, 10^3, 10^4 and 10^5 Å; THF solvent, flow rate 1 mL/min). A calibration curve prepared with narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.1-1.3) PIBs has been used.

Equipment, Major Components, Operational Parameters

A Waters Prep LC System/500 A preparative liquid chromatograph pump including a Waters RI detector and recorder was used.

Two Jordi steel columns (122 cm long, 50 cm ID, total volume 2 x 2395 cm^3) in series packed, respectively, with 500 and 1000 Å high divinylbenzene content Styragel have been used. (The packing has been developed by Mr. H. Jordi). The mobile phase was n-hexane refluxed over CaH_2 and continuously distilled into a 5 L receiver which served as a solvent reservoir. The flow rate was 50 mL/min and the sample concentration was 5-20% w/v. The flowsheet of the assembly is shown in Figure 1. It is evident from Figure 1 that solvent is consumed only during fraction collection and wastage, otherwise it is in continuous circulation. By the use of the solvent recirculating system the equilibration of the columns, which usually takes a few hours, can be achieved without loss of solvent.

Preparative Fractionation Procedure

Efficient fractionation requires equilibrium between the mobile and stationary phases. Thus operations started by running the solvent through the system for a few hours and equilibration was indicated by a steady baseline on the recorder. Then 100 mL prefiltered (fluted filter paper) PIB solution was injected and the injection port was flushed with 50-100 mL fresh solvent. The highest and lowest molecular weight fractions indicated by the front- and tail-end of the chromatogram were discarded and the middle portion was recycled once. This "mass-shaving" was carried out at the beginning and end of a fractionation cycle, as illustrated by the chromatogram shown in Figure 2. The cut-off position of mass-shaving is mainly dictated by the shape of the GPC traces and will determine the amount of material recovered. The effluent fractions were collected by using valves (Collect Outlet A, or B on the pump) or by changing receivers manually. The PIB fractions were recovered by removing the solvent (rotavap) and the $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of the samples were determined by analytical GPC (see above).

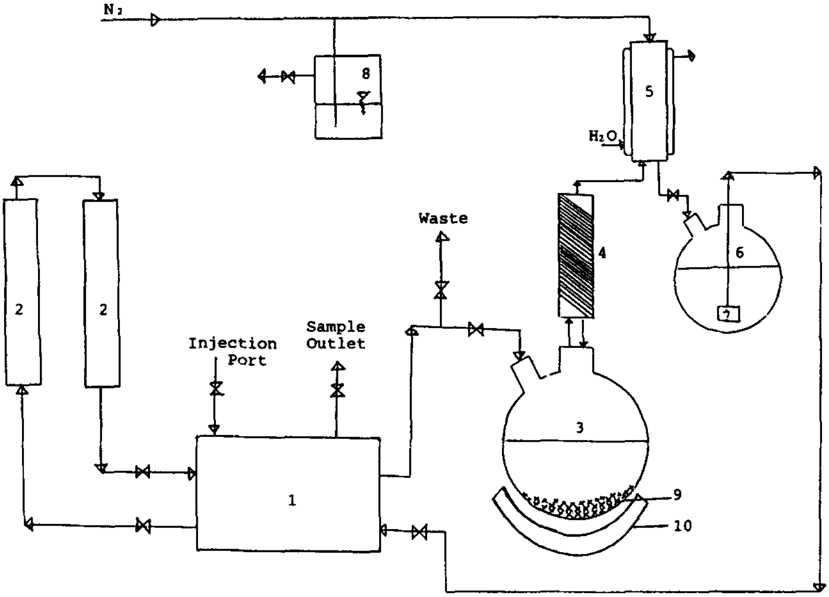

Figure 1. Flowsheet of the Prep GPC Assembly
1. Prep LC/500 A instrument with pump, RI detector, recycle/waste/collect valve and recorder
2. Columns (500, 1000 Å styragel 3. Reflux reservoir (25L) 4. Distillation column (80 cm)
5. Reflux condensor (70 cm) 6. Reservoir (5L)
7. Filter (glass frit) 8. Pressure equalizer (bubbler) 9. CaH_2 10. Heating mantle

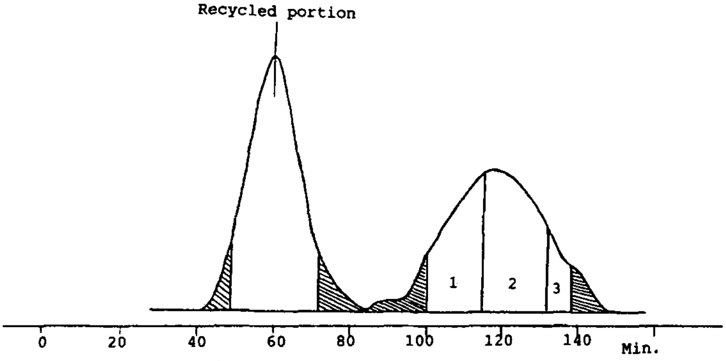

Figure 2. Representative Prep GPC Trace
////// = shaved portion, Chart speed: 10 min/cm, Relative RI response: 10, Concentration: 5% w/v, Starting PIB: M_n = 3770, MWD = 1.8

Results and Discussion

The main objective of this research was to obtain from relatively broad MWD PIBs starting materials, 10-100 g quantities of narrow MWD fractions ($\overline{M}_w/\overline{M}_n < 1.2$) by a rapid convenient routine operation. The assembly shown in Figure 1 has been used to meet this objective.

For a variety of considerations (i.e., separation mechanism, polymer solubility, availability, cost) we have selected Styragel as the packing material (stationary phase). A series of preliminary separation experiments with THF and n-hexane demonstrated that the latter solvent gives superior all-around performance as the mobile phase. Thus, n-hexane has a lower vapor pressure than THF which is advantageous for rapid product recovery, it is a safer and more stable solvent than THF which inevitably forms nonvolatile peroxides on prolonged use, it is a better solvent for PIB and thus gives lower solution viscosities and allows the use of higher solution concentrations, and is much cheaper than THF.

Solution recycling is the key to efficient quantitative fractionation and the Waters pump is equipped with the recycling mode. Recycling in fact increases the column length. Although increasing the number of recycles increases resolution, we have found that one recycle gives satisfactory MWD. By keeping the recycling minimum, product and time is saved, and the danger of peak overlap (i.e., decreased fractionation efficiency) is avoided.

Figure 2 shows a representative prep GPC trace and the fractions obtained as a function of time. The shaded areas indicate the fractions discarded and the numbers the three effluent fractions retained. Mass-shaving was carried out at the beginning and the end of the cycles. After removing the solvent (rotovap) the $\overline{M}_n$s of the fractions were determined by analytical GPC. Figure 3 shows the normalized analytical GPC traces of the original PIB together with those of the three fractions, and $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ values.

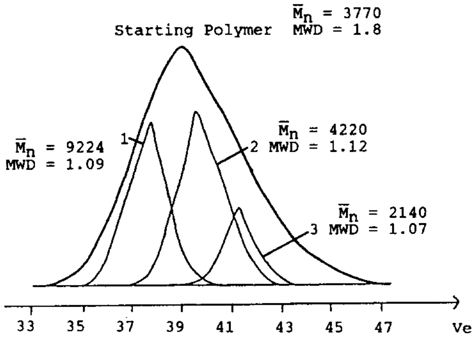

Figure 3. Normalized GPC Traces of PIB and Fractions 1,2,3

Table I illustrates the results of representative experiments in which the effects of $\overline{M}_n$, recycling, and amount of PIB loaded on M_w/M_n were investigated. Evidently very narrow

MWD ($\bar{M}_w/\bar{M}_n$ = 1.1-1.07) product was obtained with the lowest loading (5 g PIB). One recycling was sufficient to yield M_w/M_n = 1.1-1.2 under the conditions studied (60-90% total recovery). With PIB of $\bar{M}_n$ = 1880 and $\bar{M}_w/\bar{M}_n$ = 1.9 we were able to load 19 g product and still achieve M_w/M_n = 1.18-1.26. These materials can confidently be used in meaningful structure/ property characterization research.

TABLE I

Fractionation Results

Starting PIB	W_{PIB}**	Recovery %	PIB Fractions $\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
$\bar{M}_n$ = 3770	5	10	2140	2280	1.07
$\bar{M}_w$ = 6780		34	4220	4741	1.12
$\bar{M}_w/\bar{M}_n$ = 1.8		26	9224	10,055	1.09
	10	35	3410	4870	1.23
		32	8360	10,560	1.13
	*10	33	2950	4030	1.37
		30	8200	10,070	1.23
	13.5	27	2670	3210	1.20
		44	7160	8600	1.20
$\bar{M}_n$ = 1800	16	37	1520	1850	1.21
$\bar{M}_w$ = 3360		34	4010	4570	1.14
$\bar{M}_w/\bar{M}_n$ = 1.9					
	19	42	1200	1500	1.26
		44	3350	3940	1.18

* Without Recycling
**Amount of PIB Injected: g in 100 mL

An important extension of prep GPC in polymer synthesis is in the removal of low molecular weight impurities, e.g., residual initiator, additives. These low $\bar{M}_n$ components are eluted after the main PIB fraction and can be readily removed by "end-shaving". Figure 4 shows the use of this technique f for the virtually quantitative purification of a sample in one recycle: Fraction A (PIB) is recycled, fraction B (undesirable low $\bar{M}_n$ components) is rejected, fraction C (pure Fraction A) is collected.

Conclusions

We have demonstrated the use of the Waters Prep LC/System 500A (primarily recommended for the separation of small organic molecules by silica gel) in conjunction with low porosity (500 Å, 1000 Å) Styragel columns and n-hexane solvent for the efficient fractionation of low molecular weight (< 10,000) PIBs. Although n-hexane is a poor solvent to swell Styragel packings, we did not encounter any complications due to possible reverse phase chromatography during fractionation. n-Hexane was preferred as the mobile phase over THF because of its relative safety when handled in large quantities and much lower solution viscosity. Thus we were able to inject relatively large quantities (up to ~20 g/run) of PIB without increasing the injection volume and overloading the columns.

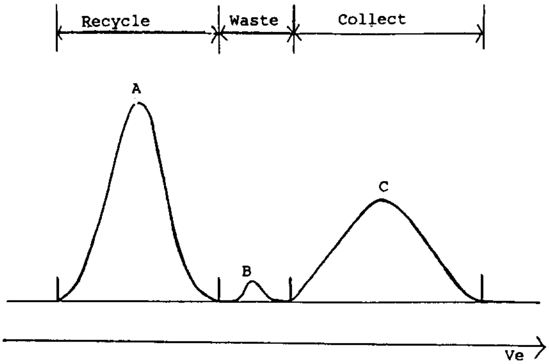

Figure 4. Purification of PIB Sample ($\overline{M}_n$ = 2500, $\overline{M}_w/\overline{M}_n$ = 1.9)

The combination of shaving masses at the tail ends and one recycling gave very good fractionation ($\overline{M}_w/\overline{M}_n$ < 1.2) of the starting broad MWDs PIBs. One recycling improves the resolution considerably and decreases solvent consumption. Under these conditions PIB fractions of $\overline{M}_w/\overline{M}_n$ < 1.2 could be routinely obtained. With lower PIB concentrations even narrower polydispersities can readily be isolated. Prep GPC is also useful for the efficient removal of low molecular weight organic impurities from PIB samples.

Acknowledgement

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References

1. A Peyrouset and R. Panaris, J. Appl. Polym. Sci., 16, 315 (1972)
2. F. Mahmud and E. Catterall in "Steric Exclusion Liquid Chromatography of Polymers". Josef Janca, ed., Dekker, N.Y., 1984, p. 365
3. M. K. Mishra and J. P. Kennedy, Polym. Bull., 17, 7 (1987)

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