Synthesis and characterization of near monodisperse oligomeric polystyrenes

M. R. Ambler, W. G. Stevenson
Chemical Development, The Goodyear Tire and Rubber Co., Akron, Ohio 44316, USA
and L. J. Fetters
The Institute of Polymer Science, The University of Akron, Akron, Ohio 44325, USA
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Oligomeric ($<10^3$) polystyrenes have been synthesized on a practical scale by the use of sec-butyllithium and triethylamine in cyclohexane. These samples were found to possess relatively narrow molecular weight distributions. The product analysis was accomplished by viscosity, vapour pressure osmometry, gel permeation chromatography and gas chromatography.

INTRODUCTION

The synthesis of near monodisperse polystyrene using organolithium initiators has been well documented[1,2]. The preparation of these narrow molecular weight distributed polymers is a result of the termination-free aspect of styrene and diene polymerizations initiated by organolithium species in inert solvents, a feature first recognized by Ziegler[3] in 1936 in the sense as described by Szwarc and coworkers[4] 20 years later for the ion-radical initiators such as sodium naphthalene. Although the synthesis of polystyrenes with near monodisperse molecular weight distributions has been described for molecular weights greater than $\sim 5 \times 10^3$ g/mol, only one effort[5] has been reported for the anionic synthesis of oligomeric ($<10^3$) polystyrene. Elution chromatography was used to characterize this material. A heterogeneity index of 1.07 was reported. The method used to achieve rapid initiation of this oligomeric polystyrene, in which n-butyllithium was the initiator, was via the addition of a small amount of tetrahydrofuran to the solution of monomer and benzene. It has been shown[6,7] that small amounts of cyclic ethers can serve to increase the rate of initiation while not affecting the chain propagation rate of styrene to an appreciable extent. This is, of course, a necessary prerequisite, i.e., $k_i \gg k_p$, for the synthesis of oligomeric material possessing a narrow distribution of molecular weights. The results of our work show that this requirement was met by using sec-butyllithium and cyclohexane with triethylamine used to accelerate the initiation reaction.

EXPERIMENTAL

The polymerizations were carried out, with stirring, in a stainless steel reactor (105 litre capacity) using a batch size of about 40 kg. The polar solvent used to accelerate the initiation reaction, the monomer, and cyclohexane were mixed prior to adding the sec-butyllithium. This solution contained 5% by wt of styrene. The initiator, 11.9% in cyclohexane, was then added. The polar solvent/initiator ratio was 2/1 for all polymerizations. The initial reactor temperature was 12°C. Upon the addition of the initiator, the temperature increased to a peak of about 24°C within 1 min. The reactions were allowed to go for about 6 min. Analysis indicated in all cases a greater than 99% conversion during this time period. During this interval the reactor contents returned to their initial temperature of 12°C. Methanol was then added to terminate the reaction. Termination by exposure of the active chain ends to the atmosphere was not carried out since this has been shown[8] to cause chain coupling and thus to distort an initially narrow molecular weight distribution.

The g.p.c. analyses were made using a Waters Model 200 unit operated with a 99/1 (v/v) chloroform/methanol mixture at 30°C with a differential refractometer detector. The column set of six, 4 ft Styragel columns with porosities of 10^2, 10^2, 10^3, 5×10^2, 10^3, 10^2 Å, had a plate count of 570 plates/ft at the 1 cm^3/min flow rate. This column set was found to provide adequate resolution over the approximate range of 10^2 to 3×10^3 molecular weight.

A polystyrene molecular weight calibration curve was calculated from a combination of (a) a universal $[\eta]M$ calibration curve generated[9] from characterized oligomers of polystyrene, polyisoprene, polybutadiene and polyethylene and (b) the following Mark–Houwink coefficients for polystyrene which had been previously determined[9] from a series of near monodisperse polystyrene oligomers in chloroform:

$$[\eta] = 1.108 \times 10^{-3} M^{0.502} \qquad 160 < M < 24\,000$$

$$[\eta] = 1.846 \times 10^{-6} M^{1.77} \qquad M < 160$$

Changes in detector response with molecular weight were determined by calculating (dn/dc) for published values[10] of density and specific volume for hexylbenzene and anionically prepared polystyrene. These data were used in correcting the g.p.c. chromatograms in the normal manner to convert chromatogram heights to wt % at each elution volume. This allowed the calculation of molecular weight distribution data.

Gas chromatographic (g.c.) analyses were carried out on a column packing of 10% OV1 on Chromosorb W with helium as the carrier gas. The Hewlett–Packard 5750 instrument was used. The molecular weights of the isolated peaks were determined by auxiliary gas chromatography/mass spectrometry analyses. Further details of the g.c. analyses will be discussed in a later article[11].

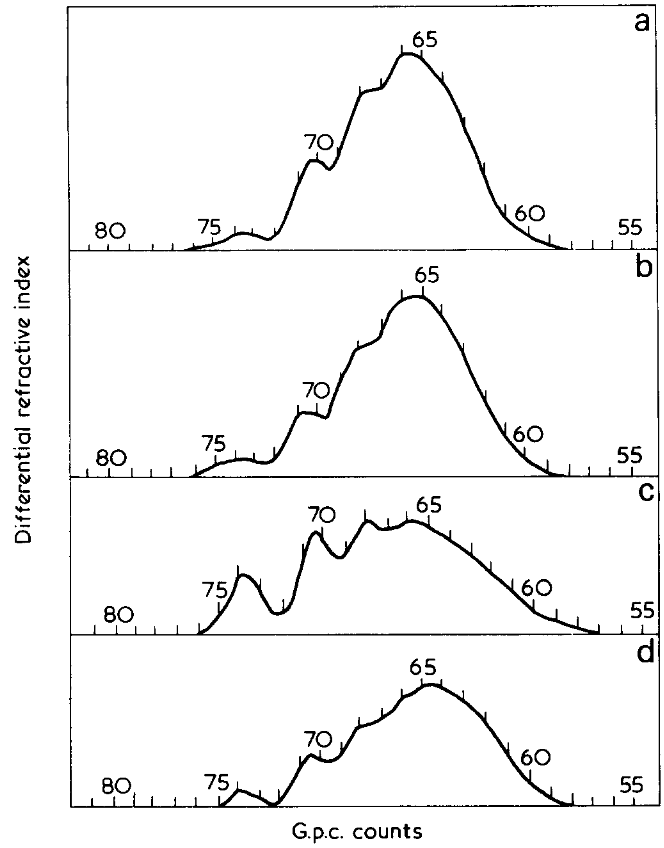

Figure 1 Gel permeation chromatographs of oligomeric polystyrenes: (a), CDS–13; (b), CDS–S–4; (c), CDS–10; (d), PC–1

Vapour pressure osmometry (v.p.o.) was carried out at 35°C in toluene. The Hitachi–Perkin–Elmer instrument was used. Intrinsic viscosity measurements were made at 30°C in a conventional viscometer. Benzene, chloroform and toluene were the solvents used.

DISCUSSION

Four oligomeric polystyrenes were examined. These included one from Pressure Chemicals Co. (PC–1) and three samples synthesized in this work. The gel permeation chromatograms of these four oligomeric polystyrenes are contained in *Figure 1*. Of the samples made in this work CDS–10 was made with dimethoxyethane as the polar cosolvent while CDS–S–4 and CDS–13 were synthesized with the aid of triethylamine as the polar promoter of the initiation reaction. It is germane to note that Quirk and Kester[12,13] have shown the solvation enthalpies of triethylamine with alkyllithiums are comparable to those values found for ethers. This indicates that triethylamine should be effective in enhancing the rate of initiation of styrene and dienes by alkyllithiums. A polar cosolvent was deemed necessary since it was observed that under our polymerization conditions sec-butyllithium alone leads to moderately polydisperse oligomeric polystyrene.

The chromatograms in *Figure 1* clearly show that none of these four oligomeric polystyrenes can be classified as 'monodisperse'. Based on the calibration curve generated for the g.p.c. column set used it was concluded that all four samples contained species ranging from the dimer* to the 11-mer. The composition analyses for these four samples are contained in *Table 1*.

The relative amount of each species determined from each chromatogram does not take into account any peak spreading which is undoubtedly present. Corrections for peak spreading were not attempted since, in our opinion, no truly reliable method exists which would allow us to determine the relative extent of peak spreading for the oligomeric species present in these samples. Nonetheless, although not monodisperse, the four samples examined by g.p.c. do possess relatively narrow molecular weight distributions, which are close to the predicted values of the Poisson distribution[14] (DP_w/DP_n = 1.16 for DP_n = 6) for these oligomeric samples.

Additional insight into the distribution of the oligomeric species in CDS–S–4 was achieved by gas chromatography. These data are presented in *Table 2*. It should be noted that two important differences can be seen between the g.p.c. and g.c. data:

(a) g.p.c. suggests the presence of both 10- and 11-mer species while g.c. shows the highest molecular weight oligomer to be the 9-mer;

(b) the g.p.c. and g.c. data fail to agree, in the main, on the relative amounts of each species present in the CDS–S–4 sample. We believe that these differences are ascribable to peak spreading in the g.p.c. and potential errors in the refractive index correction applied to each oligomeric species present. It should be noted that, unlike g.p.c., the g.c. results showed nine well resolved peaks, which is in sharp contrast to the peak spreading which occurs in the g.p.c. measurement. Our experiences thus far indicate that for oligomeric materials more accurate insight into the relative amounts of each species can be obtained from g.c. measurements as compared with g.p.c. analysis. This topic will be discussed in greater detail in a later paper[11].

However, in spite of differences, both g.p.c. and g.c. give essentially similar values for $\bar{M}_n$ and $\bar{M}_w$ for CDS–S–4. These data are contained in *Table 3* along with the characterization data obtained for the other three oligomeric polystyrenes.

Table 1 Composition (wt%) of oligomeric polystyrenes from g.p.c. measurements

DP_n	M_i	PC–1	CDS–10	CDS–S–4	CDS–13
2	266	4.2	13.0	2.6	3.6
3	370	11.2	18.4	11.4	13.6
4	474	16.2	18.3	21.0	22.4
5	578	18.5	16.9	26.6	24.6
6	682	19.3	13.4	17.2	16.4
7	786	14.8	8.5	9.6	10.5
8	890	8.3	5.9	6.0	4.5
9	994	4.4	2.9	3.4	3.3
10	1098	2.7	1.9	1.5	1.1
11	1202	0.4	0.8	0.5	–

Table 2 Characterization of oligomeric polystyrene CDS–S–4 by gas chromatography

Area (%)	Molecular weight	*DP*
1.1	266	2
13.4	370	3
21.2	474	4
22.4	578	5
19.2	682	6
13.2	786	7
7.3	890	8
2.2	994	9

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* This includes the sec-butyl group from the initiator

Table 3 Molecular constants of oligomeric polystyrenes

Sample	$\bar{M}_s$[a]	$\bar{M}_n$ (v.p.o.)	$\bar{M}_n$ (g.p.c.)	$\bar{M}_n$ (g.c.)	$\bar{M}_w$ (g.p.c.)	$\bar{M}_w$ (g.c.)	$[\eta]$ (dl/g)	$[\eta]$[d] (dl/g)
PC–1	550	524 ± 7%	570	–	636	–	0.24 ± 0.001[b]	–
CDS–10	600	–	480	–	557	–	–	–
CDS–S–4	600	570 ± 8%	555	563	605	597	0.0245[c]	0.0299
CDS–13	600	520 ± 8%	535	–	588	–	0.023 [c]	0.0275

[a] Predicted number-average molecular weight based on the ratio of monomer to initiator; [b]benzene; [c]toluene; [d]chloroform

Based on the g.p.c. and g.c. results, heterogeneity indices ranging from 1.16 to 1.06 are obtained. It is clear from this work that the sec-butyllithium/triethylamine system can be used to prepare oligomeric polystyrene possessing a relatively narrow molecular weight distribution whereas the use of dimethoxyethane seemingly leads to a more polydisperse product. This may well be due to an unfavourable ratio of the rate constants of initiation and propagation under the synthesis conditions used in this work. Furthermore, the combined use of triethylamine and sec-butyllithium have led to the synthesis, on a practical scale, of oligomeric polystyrenes possessing molecular weight distributions comparable to the PC–1 polystyrene.

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REFERENCES

1 See appropriate references in Morton, M. and Fetters, L. J. *Rubber Rev.* 1975, **48**, 359

2 Fetters, L. J. and Morton, M. 'Macromolecular Synthesis', (Ed. W. J. Bailey), Wiley, New York, 1972, p 77

3 Ziegler, K. *Angew. Chem.* 1936, **49**, 499

4 Szwarc, M. *Nature,* 1956, **178**, 1168; Szwarc, M., Levy, M. and Milkovich, R. *J. Am. Chem. Soc.* 1956, **78**, 2656

5 Altares, T., Wyman, D. P. and Allen, V. R. *J. Polym. Sci. (A)* 1964, **2**, 4533

6 Bywater, S. and Worsfold, D. J. *Can. J. Chem.* 1962, **40**, 1564

7 Alexander, I. A. and Bywater, S. *J. Polym. Sci. (A)* 1968, **6**, 3407

8 Fetters, L. J. and Firer, E. *Polymer* 1977, **18**, 306

9 Ambler, M. R. *J. Polym. Sci. (Polym. Lett. Edn)* 1976, **14**, 683

10 Candau, F., Francois, J. and Benoit, H. *Polymer* 1974, **15**, 626

11 Ambler, M. R. to be published

12 Quirk, R. P . and Kester, D. E. *J. Organomet. Chem.* 1974, **72**, 623

13 Quirk, R. P. and Kester, D. E. *J. Organomet. Chem.* 1977, **127**, 111

14 Flory, P. J. *J. Am. Chem. Soc.* 1940, **62**, 1561