Polymer Bulletin 22, 471–474 (1989)

Polymer Bulletin

© Springer-Verlag 1989

Synthesis of high molecular weight near-monodisperse poly(4-methylstyrene) by anionic polymerization

Jimmy W. Mays[1,*] **and Nikos Hadjichristidis**[2]

[1]Department of Chemistry, University of Alabama at Birmingham, Birmingham, AL 35294, USA
[2]Department of Chemistry, University of Athens, GR-106 80 Athens, Greece

Summary

The synthesis of high molecular weight near-monodisperse poly(4-methylstyrene) is described. The polymerizations were conducted using sec-butyllithium as initiator and benzene as solvent. Chain transfer involving the p-methyl group is effectively prevented by the combination of low polymerization temperature (0°C) and limited (<60%) conversion.

Introduction

Anionic polymerization is presently the most widely utilized method for synthesis of well-defined, near-monodisperse, linear and branched polymers and copolymers (1-4). A large number of monomers (1,2) are, under appropriate conditions, polymerized in a termination-free manner ("living" polymerization).

The polymerization of 4-methylstyrene by anionic polymerization, has not been studied much, in part because of potential chain transfer reactions involving the initiator or growing chain ends and the p-methyl groups of the monomer and polymer. It is pertinent to note that chain transfer to toluene (solvent) in the butyllithium initiated polymerization of styrene is well-documented (5). A very recent study (6) of chain transfer to toluene in polymerization of styrene by tert-butyllithium demonstrated that the extent of transfer is controlled by both temperature and the duration of the reaction.

We are not aware of any prior attempt to prepare high molecular weight near-monodisperse poly(4-methylstyrene) by anionic polymerization. Brower and McCormick (7) prepared a single sample of "poly(vinyltoluene)" using sodium naphthalene initiation in tetrahydrofuran (THF) at -70°C, but this resulted in a higher than theoretical molecular weight and a rather broad ratio of weight-average ($\bar{M}_w$) to number-average molecular weight ($\bar{M}_N$) of 1.25. In the following, we report the synthesis of near-monodisperse high molecular weight poly(4-methylstyrene).

Experimental

4-Methylstyrene (98%) was obtained from Aldrich and was purified by sequential exposure to and distillation from calcium hydride and dibutylmagnesium (Lithium Corporation). The pure monomer was collected in evacuated (ca. 10^{-6} mm Hg) ampoules equipped with breakseals. The monomer was stored at -78°C until use (< 72 h).

---

[*] Author to whom correspondence should be addressed

Table 1: Polymerization Conditions

Sample	[M]^a	Duration (hours)	Grams Monomer	Moles Initiator
PMS-A	10	7	8	2.7×10^{-4}
PMS-B	10	16	8	1.6×10^{-4}
PMS-C	10	16	8	9×10^{-5}
PMS-D	10	16	8	4×10^{-5}
PMS-E	40	20	17	4×10^{-5}

a) Monomer concentration (weight %).

sec-Butyllithium (Lithium Corporation) was used as initiator with benzene as solvent. The latter was purified by published methods (1). Polymerizations were conducted in sealed, evacuated reactors with breakseals at 0°C (ice bath). Termination was achieved with degassed methanol. Additional details of the polymerizations are presented in Table 1.

Polydispersities were measured via size exclusion chromatography (SEC) using a Waters model 510 pump and Waters model 410 differential refractometer with THF as the mobile phase. A flow rate of 1.0 mL/min was maintained through two Waters "linear ultrastyragel" columns (continuous porosity range of 10^2 - 10^6 Å). 20 µl of ca. 0.2% (w/v) solutions were injected. Reported polydispersities are based on a polystyrene calibration using well-characterized standards (Pressure Chemical, Goodyear, Toyo Soda, and Polymer Labs). $\bar{M}_w$ values were measured in toluene using a Chromatix KMX-6 low-angle laser light scattering unit (λ_o = 633nm) at 26°C. The refractive index increment (dn/dc) measured under the same conditions with the Chromatix KMX-16 refractometer, was 0.095 ± 0.001 mL/g. The value of dn/dc was independent of $\bar{M}_w$ for the samples studied.

Results and Discussion

Projected and measured molecular weights and polydispersities are presented in Table 2 for five poly(4-methylstyrenes) covering the molecular weight range of 10^4 - 2.4×10^5. The combined use of low polymerization temperature (0°C) and limited conversions (30-60%) for sec-butyllithium-intiated polymerization in benzene apparently limits

Table 2: Molecular Weights and Polydispersitites of Poly(4-methylstyrenes)

Sample	Conversion (%)	Theoretical^a $\bar{M}_n$ (g/mol)	LALLS $\bar{M}_w$ (g/mol)	SEC $\bar{M}_w/\bar{M}_n$	SEC $\bar{M}_z/\bar{M}_w$
PMS-A	30	8,900	9,500	1.03	1.03
PMS-B	38	19,000	20,600	1.03	1.02
PMS-C	39	35,000	38,900	1.03	1.03
PMS-D	31	62,000	66,000	1.04	1.02
PMS-E	59	251,000	242,000	1.05	1.03

a) (Grams monomer/moles initiator) x conversion.

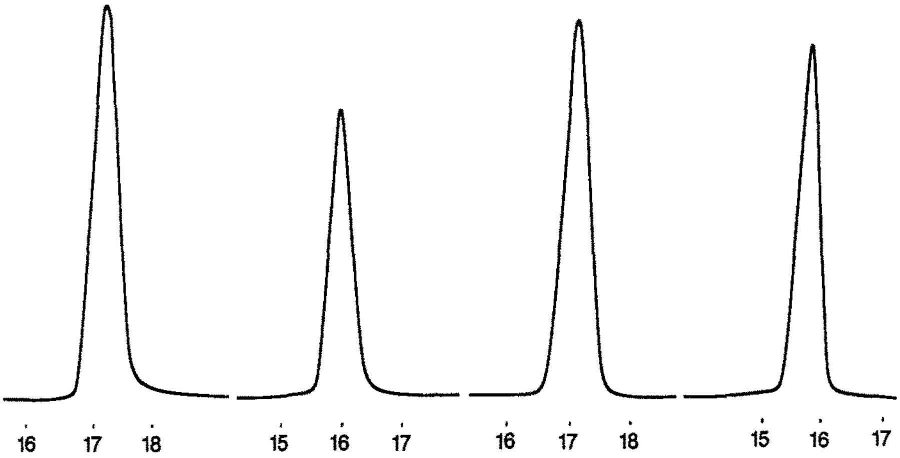

Figure 1: SEC chromatograms of Poly(4-methylstyrenes) and commercial polystyrene standards. From left to right are PMS-D, PMS-E, and polystyrene standards of 50,000 and 207,000 in molecular weight. Polydispersities of all four samples are extremely low (see Table 2).

the extent of chain transfer. Not only are polydispersity ratios extremely low (see Figure 1 for a comparison with commercial polystyrene standards), but, after taking into account the limited conversion, theoretical and experimental molecular weights are also in close agreement. These results suggest the absence of detectable amounts of chain transfer to both monomer and polymer, either of which would lead to broadening of the molecular weight distribution.

Our results for butyllithium-initiated polymerization of 4-methylstyrene appear to fortify the findings of Wang et al. (6) regarding effects of temperature and conversion on the closely related chain transfer reaction involving toluene. It is our opinion that even higher molecular weight poly(4-methylstyrenes) with extremely narrow molecular weight distributions could be prepared using the methods cited herein. We have no attempt, thus far, to achieve quantitative conversion to polymer in these systems. This will be done in future work. Nevertheless, based on the findings reported herein, it should now be possible to synthesize well-defined block copolymers incorporating poly(4-methylstyrene) segments, so long as this is the last monomer to be added.

Acknowledgement

JWM acknowledges with gratitude support by the Petroleum Research Fund, administered by the American Chemical Society.

References

1. Morton M, Fetters LJ (1975) Rubber Revs 48: 359
2. Morton M (1983) Anionic polymerization: Principles and practice. Academic, New York
3. Rempp P, Franta E, Herz JE (1988) Adv Polym Sci 86: 146
4. Quirk RP, Kinning PJ, Fetters LJ (1989) Block Copolymers. In: Aggarwal SL (ed.) Comprehensive Polymer Science, vol 7. Pergamon, Oxford
5. Gatzke AL (1969) J Polym Sci: Part A-1 7: 2281
6. Wang LS, Favier JC, Sigwalt P (1989) Polymer Comm 30: 248
7. Brower FM, McCormick HW (1963) J Polym Sci: Part A 1:1749

Accepted November 3, 1989 K