

Efficient Syntheses of the Triblock Copolymer Styrene-*b*-Tetrahydrofuran-*b*-Styrene by Coupling of Preformed Blocks

JAMES C. W. CHIEN, JIN-LONG HONG, and C. PETER LILLYA,*
*Department of Chemistry, Department of Polymer Science and Engineering,
University of Massachusetts, Amherst, Massachusetts 01003*

Synopsis

The triblock copolymer styrene-*b*-tetrahydrofuran-*b*-styrene was prepared from commercially available hydroxyl-terminated poly(tetrahydrofuran), $M_n = 1,650$ and mono-hydroxyl-terminated polystyrene, $M_n = 7,600$. Poly(tetrahydrofuran) blocks were first chain extended by reaction with 1.1 equivalents 4,4'-diphenylmethane diisocyanate (MDI) and subsequently end capped with 20% excess of hydroxyl-terminated polystyrene. Gel permeation chromatography revealed clearly the success of the end capping step to give triblock copolymer mixed with a small amount of excess polystyrene. $^1\text{H NMR}$ revealed a gross composition by weight of 50% styrene, 41% tetrahydrofuran, and 9% MDI. DSC revealed a 5°C elevation of the PTHF glass transition and a 15°C lowering of PS glass transition temperature as compared with those of the individual component blocks. These values along with behavior of films as a tough elastomer are consistent with triblock structure and microphase separated morphology. The polymer does not flow readily below 125°C which is well above T_g of the polystyrene domains.

INTRODUCTION

The literature contains reports of a variety of syntheses of block copolymers of polystyrene and polytetrahydrofuran. The earliest report of styrene-*b*-tetrahydrofuran-*b*-styrene (S*b*THF*b*S) is that of Furukawa et al.¹ who generated radical initiator sites at the ends of poly(tetrahydrofuran) (PTHF) blocks in the presence of styrene monomer. The production of homopolystyrene (PS), deactivation of chain ends by abstraction of active hydrogen, and other side reactions gave a mixture of products which nevertheless exhibited reasonable mechanical properties.

Synthesis of styrene-tetrahydrofuran block copolymers has served as a test problem for a number of groups investigating techniques for reversal of charge in chain polymerization. This has been achieved by changing from anionic to cationic²⁻⁵ and cationic to anionic^{4,6,7} mechanisms. Three reports^{2,4,7} describe the triblock S*b*THF*b*S, but no description of mechanical properties are offered though Zang et al. report some for a methyl methacrylate triblock.⁷ In no case is a clean syntheses of "pure" triblock demonstrated. Inefficient initiation from functionalized chain ends^{2,6} and stoichiometric requirements leading to considerable homopolymer production⁴ are typical problems.

The most elegant syntheses involve reaction of living polystyrene anion (PS⁻) with living THF dication.^{8,9,10} This coupling, which is inefficient for poly- α -methylstyrene living anion,¹¹ is very efficient in the case of PS⁻. Both

* To whom correspondence should be addressed.

Smith⁸ and Richards⁹ describe clear evidence for clean synthesis of triblock. Smith reports a narrow molecular weight distribution of 1.09 while Richards that coupling at PTHF⁺ chain ends is $\geq 90\%$ and at PS⁻ chain ends is $\geq 95\%$. Absence of diblock impurities from monofunctional PTHF monocation or inefficient coupling cannot be demonstrated, however. No nonsolution properties are described for these polymers.

Our interest in thermoplastic elastomers with flow temperatures near 100°C led to an interest in SbTHFbS which should flow above the polystyrene T_g . Because low melt viscosity was also a target, we decided to test the mechanical properties of a relatively low molecular weight triblock. Coupling of living polymers is the method of choice for synthesis of triblock with block weights in excess of 20,000, but it occurred for us that lower molecular weight SbTHFbS might be assembled by coupling readily available pre-assembled blocks, avoiding the requirement of handling large quantities of living ionic polymer. We report below successful synthesis of SbTHFbS from monohydroxyl-terminated polystyrene ($M_n = 7,600$) (PS-OH) and polytetrahydrofuran diol (HO-PTHF-OH) by coupling with 4,4'-diphenylmethane diisocyanate (MDI). The triblock is obtained as a mixture with a small amount of PS-OH.

EXPERIMENTAL

General

Infrared spectra were recorded with a Perkin Elmer 1420 spectrometer and calibrated using the 1601 cm^{-1} band of polystyrene. NMR samples were dissolved in CDCl_3 with internal tetramethylenesilane standard, and spectra were obtained using a Varian Associates XL-300 instrument. Gel permeation chromatography was carried out with a Waters Associates model 201 instrument using a standard Styragel four-column set with 500, 10^3 , 10^4 , and 10^5 Å pore size employing THF as solvent. Columns were calibrated using standard polystyrene samples. Polymer thermal transition temperatures were determined on a Perkin-Elmer model DSC-2 differential scanning calorimeter with a Thermal Analysis Data Station at a heating rate of 20°C/min.

Styrene (150 mL) was purified by washing once with 50 mL of 10% aq. NaOH, twice with 25 mL of H_2O , once with 50 mL of sat. aq. NaCl. Washed styrene was mixed with CaH_2 , degassed by five freeze-pump-thaw cycles, and then distilled from the CaH_2 into a sealed container for storage. Cyclohexane was refluxed with CaH_2 and distilled under argon into a storage vessel where it was degassed by five freeze-pump-thaw cycles.

Monohydroxyl-Terminated Polystyrene

Polymerization was carried out in a 500 mL round-bottom flask with a side-arm connected to a nitrogen gas inlet and vacuum system through a three-way stopcock. This reaction vessel was flushed and evacuated with prepurified nitrogen gas six times before reagent transfer. Cyclohexane, (200 mL) prepurified by the above procedure, was added to the reaction vessel via cannula. To the nitrogen-blanketed, magnetically stirred cyclohexane solvent, styrene (88.92 g) was introduced directly followed by 10 mL of *s*-butyllithium (1.1 M as de-

terminated from titration with $\text{Ph}_2\text{CHCO}_2\text{H}^{12}$) to initiate the polymerization. The flask was heated at 70°C for 3 h, then cooled to room temperature. Twice the theoretical amount of ethylene oxide was dropped into the reaction mixture via cannula to cap the anionic chain ends. After the reaction mixture was stirred overnight, polymer was precipitated three times by addition of methanol to a cyclohexane solution. The resulting polymer was allowed to stand in benzene over a 3A Molecular Sieve for 24 h. Azeotropic distillation with benzene was carried out to remove traces of water, and the remaining benzene was removed on a rotary evaporator followed by vacuum distillation at 100°C (1 Torr) overnight. A yield of 85.36 g (96%) monohydroxyl-terminated polystyrene was obtained.

Molecular weight was determined from GPC ($M_n = 7,620$; $M_w = 8,150$; $D = 1.07$). The equivalent weight determined from Carl-Fischer titration¹³ was $7,390 \pm 70$. Combination of M_n and hydroxyl number gave a functionality of 0.97.

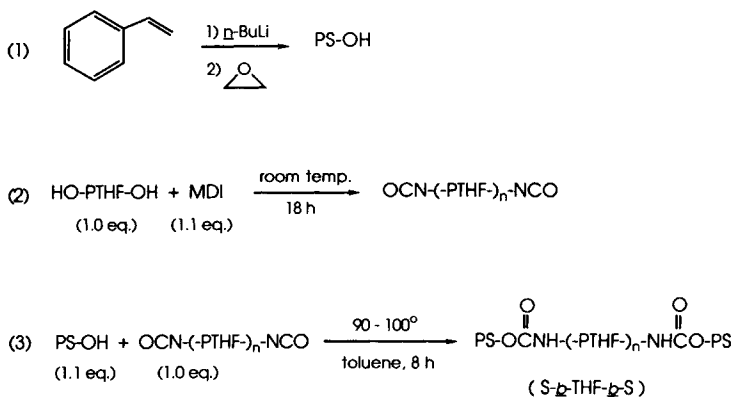
*Synthesis of Styrene-*b*-Tetrahydrofuran-*b*-Styrene Triblock Copolymer*

Poly(tetrahydrofuran) diol ($M_n = 1,650 \pm 8$; 2.1793 g, 0.264 meq of OH) was mixed with 0.3600 g of MDI (0.288 meq of NCO) and 2 mL of toluene in a three-neck, round-bottom flask with argon gas inlet and outlet tubes and mechanical stirrer. End-capping was conducted at room temperature for 18 h in the presence of catalyst (0.04 g of dibutyltin dilaurate). After the reaction mixture was warmed to 90 – 100°C , excess PS-OH (2.150 g, 0.0290 meq of OH; $M_n = 7,390 \pm 70$) in 10 mL of toluene was added. IR spectroscopy was used to monitor the coupling reaction by following the isocyanate absorption at 2270 cm^{-1} . After 8 h, the reaction was stopped; purification was achieved by precipitating the resulting polymer with MeOH from toluene solvent to give 2.420 g (90%). Copolymer films cast by slow evaporation of toluene solutions were tough and transparent. A separate sample of PTHF prepolymer from reaction of PTHF with MDI was prepared for DSC analysis.

RESULTS AND DISCUSSION

Synthesis

Synthesis of S-*b*-THF-*b*-S is shown in the Scheme 1. A polystyrene M_n of 8,000 was selected as a target with the goal of achieving $T_g \sim 90^\circ\text{C}$.¹⁴ Butyllithium-initiated polymerization in cyclohexane gave polystyryllithium which was capped with 2 eq. ethylene oxide to give PS-OH ($M_w = 8,150$, $M_n = 7,600$, $M_w/M_n = 1.07$). Determination of hydroxyl groups combined with the M_n value above gave a functionality of 0.97 ± 0.05 . Tetrahydrofuran diol ($M_n = 1,650 \pm 20$) was chain chain extended by coupling with 1.1 eq. MDI at room temperature in the presence of dibutyltin dilaurate catalyst. The reaction was allowed to proceed for several hours after the isocyanate IR band intensity ceased to diminish. Monitoring by GPC showed that molecular weight had ceased to increase, and that no unreacted MDI was present. This stoichiometry will give an average degree of polymerization of 21 at 100% reaction¹⁵ which corresponds to an average chain of ten PTHF and eleven MDI units.



Scheme 1. Synthesis of styrene-*b*-tetrahydrofuran-*b*-styrene copolymers.

Coupling of PS-OH with the chain ends of chain extended PTHF was conducted with 10% excess PS-OH to avoid the presence of diblock, S-*b*-THF, which would lead to loss of good mechanical properties.¹⁶ Coupling, monitored by decrease of isocyanate (2270 cm^{-1}) and -OH ($3650\text{-}3380\text{ cm}^{-1}$) band in infrared intensity and appearance of isocyanate NH (3300 cm^{-1}) and C=O (1700 cm^{-1}) infrared bands. At $60\text{-}70^\circ\text{C}$ coupling was slow, but at $90\text{-}100^\circ\text{C}$ isocyanate absorption disappeared after only 6 h. Polymer was isolated after methanol quench by precipitation from toluene. An attempt to remove excess PS-OH based on differential solubility in hexane was unsuccessful.

GPC Analysis

GPC curves of different samples are shown in Figure 1, where $\text{OCN-(PTHF)}_n\text{-NCO}$ designates the PTHF prepolymer, PTHF ($M_n = 1,650 \pm 8$) chain extended with 1.1 eq of MDI. $\text{OCN-(PTHF)}_n\text{-NCO} + \text{PS-OH}$ designates an uncoupled mixture of PTHF prepolymer with PS-OH in a weight ratio equal to that used to synthesize triblock. The analysis below shows that efficient coupling was achieved.

The major difference between block copolymer and mixtures of PS and PTHF prepolymer is the relative intensities of the peaks centered at 29–30 mL and 32.5 mL. The peak which eluted at 32.5 mL belongs to PS-OH, as demonstrated by its separate injection. In the case of mixture $\text{OCN-(PTHF)}_n\text{-NCO} + \text{PS-OH}$, the peak eluted at 29 mL is PTHF prepolymer which exhibited a characteristic low detector response compared to PS-OH. The UV detector operated at 254 nm, thus detector response will be proportional to sample absorptivity at 254 nm. Polystyrene, which contains one aromatic ring per repeat unit, exhibits higher absorption intensity than PTHF prepolymers where the only source for UV absorption is the aromatic rings in the MDI linkages. If the coupling reaction did proceed, we would expect increased detector response in the high molecular weight region due to the incorporation of polystyrene blocks with PTHF prepolymer. This is what we observed in the GPC curve of triblock copolymer. The small peak at 32.5 mL is the excess PS-OH. The large fraction of total detector response associated with the 29–30 mL peak demonstrates the

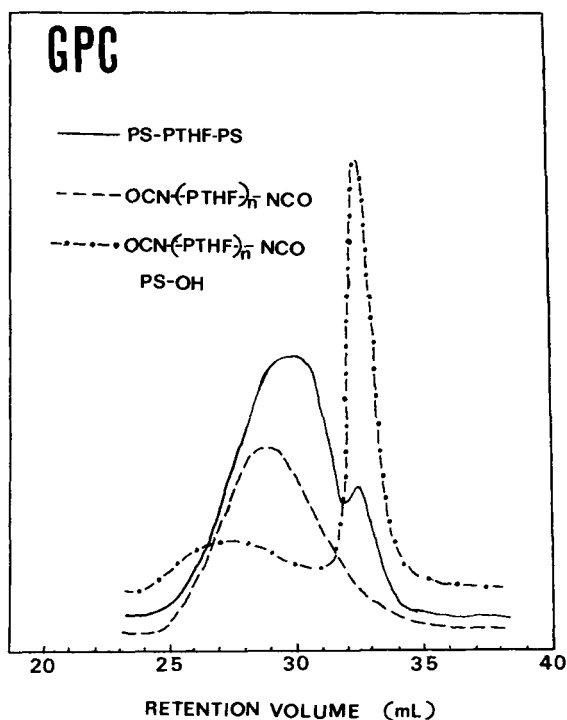


Fig. 1. Gel permeation chromatograms of triblock copolymer, PTHF prepolymer, and a mixture of PS—OH and PTHF prepolymer.

efficiency of coupling. Thus, while attachment of PS blocks to the ends of PTHF prepolymer appears not to affect the hydrodynamic radius of the polymer in the THF eluent, it is clear that coupling has occurred.¹⁷

¹H-NMR Spectroscopy

¹H-NMR signals for the polymer and their assignments are listed in the Table. Assignment of the 3.8 ppm singlet to the MDI methylene was based upon comparison with analogs.¹⁸ Comparison of the relative intensities of signals

TABLE I
H¹ Signal Assignments and Intensities for S-*b*-THF-*b*-S Triblock Copolymer in CDCl₃^a

| δ (ppm) | Assignment | Relative intensity |
|-------------------|---|--------------------|
| 1.2-2.2 | β -CH ₂ to oxygen in PTHF block | 16.0 |
| | α -CH and β -CH ₂ to phenyl group in PS block | |
| 3.4 | α -CH ₂ to oxygen in PTHF block | 10.0 |
| 3.8 | CH ₂ in MDI linkage | 0.31 |
| 4.2 | NH in urethane group | 0.49 |
| 6.2-7.8 | Aromatic protons in PS block and MDI units | 12.0 |

^a At 300 MHz.

at 1.2–2.2, 3.4, 3.8, and 6.2–7.8 ppm yielded a polymer composition by weight of 50% styrene, 41% THF and 9% MDI ($\pm 3\text{--}4\%$). The styrene content is slightly higher than that in the feed (46%).

Differential Scanning Calorimetry

Microphase separation in analogous PEO–PS block copolymers leading to distinct PTHF and PS glass transitions has been reported.¹⁹ Both our triblock and PTHF prepolymer exhibited glass and melting transitions (Fig. 2). Only the prepolymer exhibited a strong crystallization exotherm. The enthalpy of crystallization per unit PTHF for triblock copolymer is much lower than that for PTHF prepolymer. Physical crosslinks in microphase separated triblock copolymer restrict mobility of PTHF segments and could interfere with the crystallization process. Ideally, the heat capacity of a completely phase-separated block copolymer should be proportional to the weight fraction of the contributing block in the copolymer. Therefore, we may calculate the heat capacity of THF block in a completely phase-separated S-*b*-THF-*b*-S as 0.125 cal/g deg (heat capacity of PTHF prepolymer) $\times 0.41 = 0.051 \text{ cal/g deg}$. This is close to the experimental value of 0.055 cal/g deg . Agreement indicates good phase separation exists in this triblock copolymer. There is also a small variation of the glass transition temperature between PTHF prepolymer (-75°C) and triblock copolymer (-70°C). The higher glass transition temperature in triblock copolymer, in which all PTHF chain ends are tethered, is expected.

Glass transition temperatures of styrene in PS–OH and triblock copolymer appeared at 89°C and 74°C , respectively. The glass transition temperature of PS–OH is, therefore, reduced to a lower value after being incorporated with PTHF block. This transition in the triblock copolymer was too weak and broad to permit accurate determination of heat capacity. The observations above are consistent only with a high degree of microphase separation.

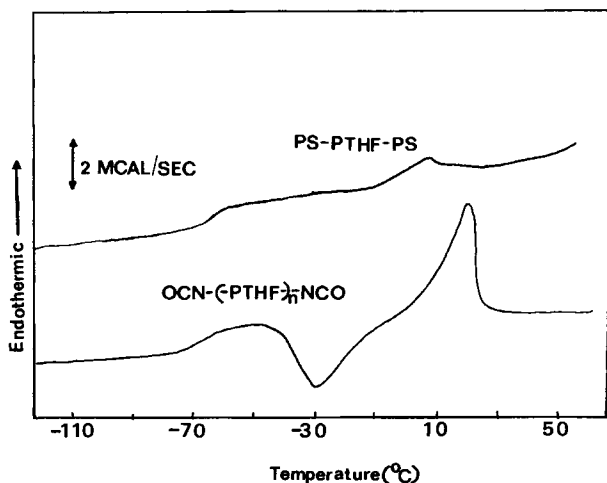


Fig. 2. Low temperature differential scanning calorimetry traces for triblock-copolymer and PTHF prepolymer.

Physical and Mechanical Properties

Further evidence for successful coupling at 90–100°C was obtained by qualitative observations of product properties. The product of attempted coupling at 60–70°C was an inhomogeneous, white solid. The weakness of film samples under stress suggests the absence of triblock structure or the presence of considerable diblock impurity. In contrast, copolymer produced at 90–100°C formed a transparent homogeneous film which behaved as a tough elastomer.

A triblock sample of 1 mm thickness and 50 mm diameter was placed between parallel rheometer plates and heated in a nitrogen atmosphere. Despite its T_g value of 74°C it failed to flow until the temperature reached 125°C. At this temperature it is a clear viscous liquid. Apparently, the softening temperature of triblock copolymer is well above the glass transition of its styrene hard block. A dramatic lowering of viscosity at the glass transition is not observed for this triblock copolymer. Subsequent GPC analysis of a small portion of heated polymer (130°C for one hour) showed no evidence for degradation.

CONCLUSION

This work clearly demonstrates the feasibility of the prepolymer coupling strategy for syntheses of low molecular weight thermoplastic elastomers. The synthesis could be easily conducted on large scale in a single pot. No lower limit can be placed on diblock content. However, the physical and mechanical properties of the triblock copolymer are consistent only with a triblock structure with microphase separation which leads to physical crosslinking and elastomeric behavior.

This work was supported by the Office of Naval Research. Assistance of Dr. Kevin Sheehan in synthesis of hydroxyl-terminated polystyrene is gratefully acknowledged.

References

1. J. Furukawa, S. Takamori, and S. Yamashita, *Die Angew. Makromol. Chem.*, **1**, 92 (1967).
2. F. J. Burgess, A. V. Cunliffe, J. R. MacCallum, and D. H. Richards, *Polymer*, **18**, 719, 726, 735 (1977).
3. D. H. Richards, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **25**, 216 (1984), and references therein.
4. M. Kucera, Z. Salajka, and P. Hudec, *Polymer*, **26**, 1732 (1985), and references to previous work.
5. Y. Yagci, *Polym. Commun.*, **27**, 21 (1986).
6. P. Cohen, M. J. Abadie, F. Schue, and D. H. Richards, *Polymer*, **23**, 1105 (1982).
7. X. Zang, H. Zhang, and X. Feng, *Gaofenzi Tongxun*, **5**, 375 (1983); *C.A.*, **100**, 176217y (1985).
8. S. Smith and A. J. Hubin, *J. Macromol. Sci., Chem.*, **A7**, 1399 (1973).
9. D. H. Richards, S. B. Kingston, and T. Souel, *Polymer*, **19**, 68 (1978).
10. K. Ishizu and T. Fukutomi, *J. Polym. Sci., Part A, Polym. Chem.*, **25**, 23 (1987).
11. D. H. Richards, S. B. Kingston, and T. Souel, *Polymer*, **19**, 806 (1978).
12. W. G. Kofran, L. M. Baclawski, *J. Org. Chem.*, **41**, 1879 (1976).
13. G. A. Stenmark and F. T. Weiss, *Anal. Chem.*, **28**, 1784 (1956).
14. J. Brandrup, E. H. Immergut, and W. McDowell, Eds., *The Polymer Handbook*, Wiley, New York, NY, 1975, p. III-131.
15. G. Odian, *Principals of Polymerization*, 2nd ed., Wiley, New York, 1981, p. 84.

16. M. Morton in *Encyclopedia of Polymer Science and Technology*. N. M. Bikales, Ed., Interscience, New York, vol. 15, p. 527-529, and A. Noshay and J. E. McGrath, *Block Copolymers; Overview and Critical Survey*, Academic Press, New York, 1977, p. 224.

17. Analysis of products of attempted coupling at 60-70° gave traces similar to those for the PTHF-PS-OH mixture.

18. Cf. *p-R-C₆H₄CH₂C₆H₄-p-R*: *R* = OCH₃, $\delta(\text{CH}_2) = 3.79$ ppm, *R* = NH₃⁺ Cl⁻, $\delta(\text{CH}_2) = 4.07$ ppm and *R* = COCH₃, $\delta(\text{CH}_2) = 4.09$ ppm, Sadtler Standard Spectra, Sadtler Research Laboratories, Inc., Philadelphia, PA, 19104; spectra 2641*M*, 14566*M*, and 13,688*M*, respectively.

19. J. T. O'Malley, R. C. Crystal, and P. F. Erhardt, in *Block Copolymers*, S. L. Aggarwal, Ed., Plenum Press, New York, 1970, pp. 163, 179, 195.

Received February 22, 1989

Accepted July 13, 1989