Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Ramakrishnan, A. and Dhamodharan, R.(2000) 'A NOVEL AND SIMPLE METHOD OF PREPARATION OF POLY(STYRENE-B-2-VINYLPYRIDINE) BLOCK COPOLYMER OF NARROW MOLECULAR WEIGHT DISTRIBUTION: LIVING ANIONIC POLYMERIZATION FOLLOWED BY MECHANISM TRANSFER TO CONTROLLED/"LIVING" RADICAL POLYMERIZATION (ATRP)', Journal of Macromolecular Science, Part A, 37: 6, 621 — 631

To link to this Article: DOI: 10.1081/MA-100101113

URL: http://dx.doi.org/10.1081/MA-100101113

J.M.S.—PURE APPL. CHEM., A37(6), pp. 621–631 (2000)

A NOVEL AND SIMPLE METHOD OF PREPARATION OF POLY(STYRENE-B-2-VINYLPYRIDINE) BLOCK COPOLYMER OF NARROW MOLECULAR WEIGHT DISTRIBUTION: LIVING ANIONIC POLYMERIZATION FOLLOWED BY MECHANISM TRANSFER TO CONTROLLED/"LIVING" RADICAL POLYMERIZATION (ATRP)

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Key Words: Phrases, Living Anionic Polymerization, Atom Transfer Radical Polymerization, Block Copolymer, Styrene, 2-Vinylpyridine, Polymer Synthesis

ABSTRACT

A novel and simple method of preparation of a block copolymer of styrene and 2-vinylpyridine with narrow molecular weight distribution is reported. The novelty lies in the transformation of the polymerization mechanism from living anionic to controlled/"living" radical polymerization (ATRP). Thus, anionic polymerization of styrene is carried out in benzene using *sec*-butyllithium as the initiator followed by termination with ethylene oxide to prepare hydroxy-terminated polystyrene (PS-OH).

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PS-OH is converted to chloride-terminated polystyrene (PS-Cl) by a displacement reaction involving thionyl chloride and pyridine in benzene. PS-Cl is used to initiate the heterogeneous ATRP of 2-vinylpyridine in p-xylene with CuCl/2,2'-bipyridine system. The polymers synthesized are characterized by gel permeation chromatography (GPC), thin layer chromatography (TLC), IR and proton NMR spectroscopies.

INTRODUCTION

Living anionic polymerization [1] and more recently controlled/"living" radical polymerizations [2] enable the synthesis of polymers of well-defined architecture with a high degree of control over the molecular weight, molecular weight distribution and functionality. Thus, it is has been possible to synthesize a wide variety of polymer architectures including triblock, diblock, random copolymers and telechelics in narrow molecular weight distribution for various physical property studies. Block copolymers of styrene and 2/4-vinylpyridine constitute a very important class of polymers, as they are important model polymers for the investigations concerned with interfacial mechanical property enhancement and the mode of enhancement (strength and failure mechanism) of immiscible homopolymers of styrene and vinylpyridine, as well as in the experimental investigation of polymer adsorption [3-8]. The block copolymers used in these studies are synthesized by living anionic polymerization of the monomers in tetrahydrofuran (THF) at -78°C under stringent conditions involving the exclusion of oxygen and moisture in the system. The polymerization of styrene is easily accomplished at ambient to reasonably high temperatures in hydrocarbon solvents. The block copolymer synthesis of styrene with vinylpyridine requires the use of THF as the solvent, since the homopolymer of 2-vinylpyridine is insoluble in hydrocarbon solvents except at high temperatures. However, at high temperatures chain transfer competes with chain propagation. Moreover, polymerization in THF requires that it be carried out at –78°C to ensure minimum or no chain transfer to the solvent and to minimize the competing addition across the –C=N in the monomer. When all the precautions are taken, narrow dispersed block polymers of styrene and vinylpyridine can be prepared.

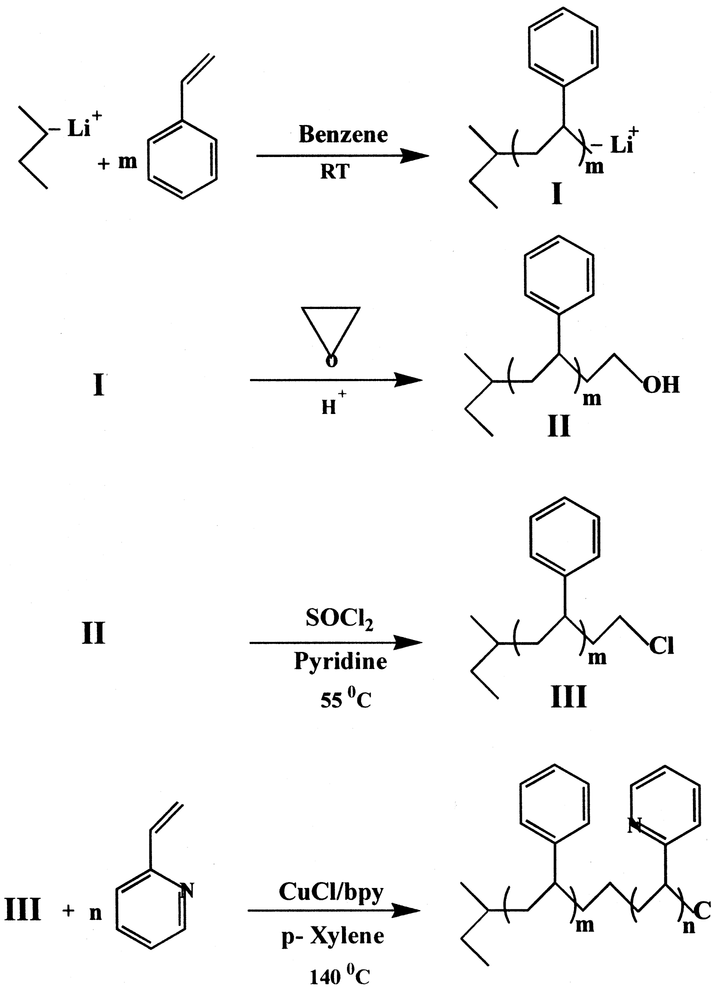
Polydispersed block copolymers of styrene and vinylpyridine can complicate the interpretation of physical properties such as interfacial mechanical property enhancement, obtained from experiments. For example, the fracture mechanism has been known to change from chain pull-out to chain scission to crazing depending on molecular weight when narrow dispersed samples are used [3]. Until recently, anionic polymerization with its demanding experimental requirements has been the only polymerization method used for the preparation of these important model systems. Recently, the transition metal catalyzed atom transfer radical polymerization (ATRP) [9] has emerged as a simple system for the synthesis of narrow dispersed polymers of various chain architectures. Several homogeneous and heterogeneous transition metal systems are available for the preparation of polymers [10]. Thus, under conditions similar to those used for free radical polymerization, polystyrenes [11a], polymethacrylates [11b], polyacrylates [11c] poly(2-hydroxypropylmethacryl-amide), poly-acrylonitrile [11d] and their block copolymers [12] (butylacrylate-styrene, methylacrylate-styrene, 2-ethylhexy-acrylate-acrylonitrile, styrene-acryloni-trile, styrene-dimethyl-siloxane, butylacrylate-dimethylsiloxane) have been synthesized with narrow molecular weight distribution. Mechanism transfer from ring-opening metathesis polymerization (ROMP) to ATRP [13a] and "living" carbocationic to ATRP [13b] as a route to prepare difficult block copolymers has also been demonstrated.

We are interested in the preparation of polymers of various architecture using styrene, 2-vinylpyridine and 4-vinylpyridine monomers, particularly towards the experimental investigation of polymer adsorption. We report here a simpler method of preparation of a block copolymer of styrene and 2-vinylpyridine in narrow molecular weight distribution which involves anionic polymerization of styrene followed by mechanism transfer to ATRP using the heterogeneous initiator system of PS-Cl/Cu(I)Cl/ bpy, developed by Matyjaszewski. Thus hydroxy-terminated polystyrene (PS-OH) is synthesized by the anionic polymerization of styrene in benzene using *sec*-butyl lithium as the initiator followed by termination with ethylene oxide as shown in Scheme 1. PS-OH is converted to PS-Cl by a simple displacement reaction using thionyl chloride and the telechelic initiator thus synthesized is used to polymerize 2-vinylpyridine by ATRP as shown in Scheme 1.

EXPERIMENTAL

Materials

Styrene and 2-vinylpyridine from Acros Organics (Belgium) were stirred over CaH_2, vacuum distilled and stored in a freezer at -50°C. p-Xylene and benzene (S. D. Fine Chemicals, India) was distilled from anhydrous $CaCl_2$, and



Scheme 1. Block Copolymer Synthesis by Mechanism Transfer from Anionic to ATRP

stored over molecular sieves. $SOCl_2$ was purified as reported [14]. CuCl (98%; Acros Organics, Belgium), 2,2'-bipyridine (BPY) S. D. Fine Chemicals, India) and Silica gel (Merck) were used as received.

Synthesis of Hydroxy-Terminated Polystyrene (PS-OH) By Anionic Polymerization

Hydroxy-terminated polystyrene was synthesized by the anionic polymerization of styrene in benzene using *sec*-butyllithium as the initiator followed by termination with ethylene oxide and hydrolysis, as previously reported [15].

Synthesis of Chloride-Terminated Polystyrene (PS-Cl)

To a 50 ml Schlenk flask, PS-OH (0.5 g), benzene (8.0 ml) and then pyridine (1.0 ml) were added. The above reaction mixture was stirred for 15 minutes at room temperature. After 15 minutes, $SOCl_2$ (1.0 ml) was added slowly under ice-cold conditions, and then finally, the reaction flask was shifted to an oil bath maintained at 55°C. The reaction was monitored by thin layer chromatography (TLC) with silica gel being the adsorbent and the eluent being benzene. It was observed that quantitative conversion was achieved within 72 hours for all the molecular weights studied. Following this, the reaction mixture was poured into water and the organic layer was separated and precipitated using excess methanol.

Poly(styrene-b-2-vinylpyridine) by ATRP

A 100 ml Schlenk flask was charged with copper (I) chloride and BPY. The flask was covered with septa and tied down with a copper wire. It was evacuated followed by filling with dry nitrogen and the cycle repeated three times. Following this, PS-Cl in p-xylene (degassed with nitrogen for 15 minutes) and 2-vinylpyridine (degassed with nitrogen for 15 minutes) were transferred to the flask via a cannula, under nitrogen atmosphere. Finally, the flask was shifted to an oil bath at a preset temperature of 140°C. After 24 hours, the viscous reaction mixture was diluted with THF and precipitated using excess hexane. The polymer obtained was further purified by reprecipitation and was dried by azeotropic vacuum distillation in the presence of benzene.

Measurements

Molecular weights and molecular weight distribution were determined by using a Waters GPC150 system with three ultrastyragel columns (1000, 500, and 100 Å) in series and THF as the eluent. The molecular weight calibration curve (Universal) was obtained using polystyrene standards. TLC analysis was performed on a commercial Merck glass plate coated with silica gel (0.25 mm thick). IR spectra were recorded using a Bruker IFS 66v, as well as a Shimadzu IR470 Infrared Spectrophotometer. A Hitachi R600 (60 MHz for ^1H) spectrometer was used for recording proton NMR spectra.

TABLE 1. GPC and TLC[#] Characteristics of PS-OH, PS-Cl, and P(S-b-2-VP)

E. NO.	PS-OH			PS-Cl			P(S-b-2-VP)	
	R_f	M_n	PDI	R_f	M_n	PDI	M_n	PDI
1	0.3	1110	1.06	0.87	1264	1.06	10733	1.14
2*	0.56	3718	1.04	0.96	4026	1.04	4853	1.10
3	0.46	1206	1.07	0.94	1644	1.09	19139	1.05

Conditions. E. NO 1: [2-VP] = 0.0158 mol/L, [PS-Cl] = 7.99* 10^{-5} mol/L, [PS-Cl]/[CuCl]/[bpy] = 1/2/6; E. NO 2: [2-VP] = 0.0071 mol/L, [PS-Cl] = 2.33* 10^{-4} mol/L, [PS-Cl]/[CuCl]/[bpy] = 1/2/6; E. NO 3: [2-VP] = 0.0112 mol/L, [PS-Cl] = 5* 10^{-5} mol/L, [PS-Cl]/[CuCl]/[bpy] = 1/2/6.

The R_f value of all the block copolymers were found to be zero.

* Reaction time in this case is 2 h while in all other cases it is 24 h.

RESULTS AND DISCUSSION

Hydroxy-terminated polystyrenes (PS-OH) were synthesized by the anionic polymerization of styrene in benzene as previously reported [15]. The GPC characteristics of the polymers synthesized are presented in Table 1. These polymers exhibit a low R_f value when eluted on silica gel using benzene as the solvent and show a single spot (see Table 1) while polystyrene of corresponding molecular weight shows a tendency to flow with the solvent confirming the presence of the hydroxy end-group. PS-OH was converted to PS-Cl by the displacement reaction with thionyl chloride in benzene in the presence of a catalytic amount of pyridine. The displacement reaction was followed by TLC on silica gel adsorbent with benzene as the eluent [14]. 100% displacement was confirmed when the spot due to PS-OH at an R_f value of 0.3, as in the case of entry 1 in Table 1, disappears completely and a single spot due to PS-Cl is seen at a R_f value of 0.87. All the end-group transformations were carried out until TLC characterization on silica gel/benzene system showed a single spot. The R_f value of PS-Cl samples thus synthesized were similar to that of polystyrene (see Table

1) suggesting the complete transformation of the polar -OH end-group to the non-polar -Cl end-group. The GPC characteristics of the PS-Cl synthesized are shown in Table 1 as well. The M_n of PS-Cl is marginally greater than that expected as a result of end-group transformation from -OH to -Cl. We attribute this to the change in polarity associated with the transformation. Thus, the polar -OH group might be buried inside the coil to avoid unfavorable interaction with the organic solvent resulting in smaller coil dimension, lesser hydrodynamic volume and therefore, smaller molecular weights. On the other hand, the non-linearity observed in the universal calibration curve in the low molecular weight region could also explain the increase in molecular weight. Thus, a very small difference in elution time of the order of a fraction of a second can result in a significant variation in the molecular weight. The GPC traces of PS-OH and PS-Cl corresponding to entry 1 of Table 1 are shown in Figure 1.

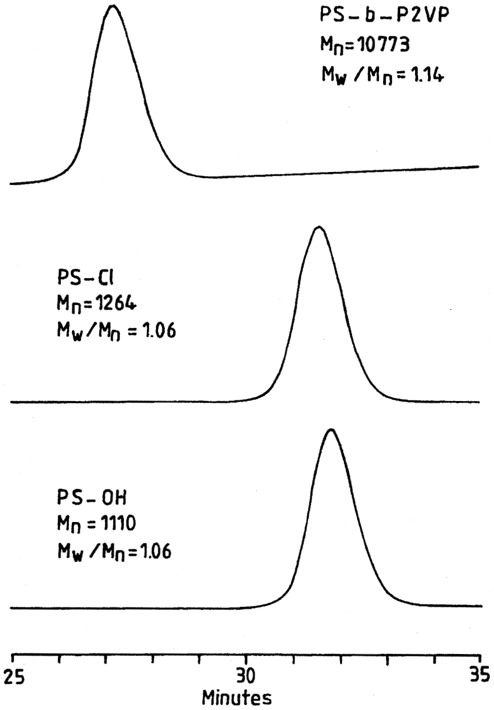


Figure 1. GPC trace of PS-OH, PS-Cl and P(S-b-2-VP).

PS-Cl thus prepared was used along with Cu(I)Cl and 2,2'-bipyridine to initiate the ATRP of 2-vinylpyridine in p-xylene under the conditions reported by Matyjaszewski. All the polymerizations were carried out for 24 hours, since we observed that this time period is required to prepare a reasonably long chain of the homopolymer of 2-vinylpyridine or 4-vinylpyridine using p-toluene-sulphonyl chloride or 2-chloroethylbenzene as the initiator in p-xylene at 140 °C. A completely methanol soluble block polymer was isolated each time. The GPC characteristics of the block copolymer are reported in Table 1 and a GPC chromatogram corresponding to entry 1 of Table 1 is shown as an example in Figure 1. The chromatogram clearly confirms the fact that a narrow dispersed block copolymer of styrene and 2-vinylpryidine can be prepared by the mechanism transfer approach. TLC of all the block copolymers on silica gel using benzene as the eluent shows a single spot with a R_f value of 0. A R_f value of 0 was observed in TLC for 2-vinylpyridine (the monomer) and 2-ethylpyridine (model compound) as well, thus confirming the fact that the block copolymer adsorbs very strongly to the silica gel from benzene.

The IR spectrum of the block copolymers is shown in Figure 2. The appearance of characteristic peaks at 3062, 3024 (aromatic C-H), 2912, 2848 (aliphatic C-H), 1594 (aromatic C=C and C=N), 1493, 1472, 1450 (backbone CH_2 bending), 756 (C-H in plane deformation of tetrasubstituted ring; 2-vinylpyridine block) and 694 (aromatic C-H in plane deformation of pentasubstituted ring; styrene block) cm^{-1} confirm the presence of styrene and 2-vinylpyridine moieties in the block copolymer as well. Further, proton NMR of the block copolymer in perdeuterated methanol confirms the formation of the block copolymer by the appearance of the characteristic peaks due to styrene and 2-vinylpyridine blocks at 6.45 (aromatic H; styrene), 7.29 (aromatic H styrene and 2-vp), and 8.17 (aromatic H 2-vp) ppm, respectively.

All the block copolymers are completely soluble in methanol, a non-solvent for polystyrene. The completele solubility in methanol, the GPC, NMR and IR data confirm that we have synthesized a narrow dispersed block copolymer of styrene and 2-vinylpyridine. Since the ATRP conditions are similar to free radical polymerization methods and therefore, are much easier to practice (the presence of moisture is tolerated) our method of preparing these model systems is simple to practice, as well as novel in nature. More detailed work regarding the kinetics of polymerization and the limits of molecular weight possible under these conditions are under investigation.

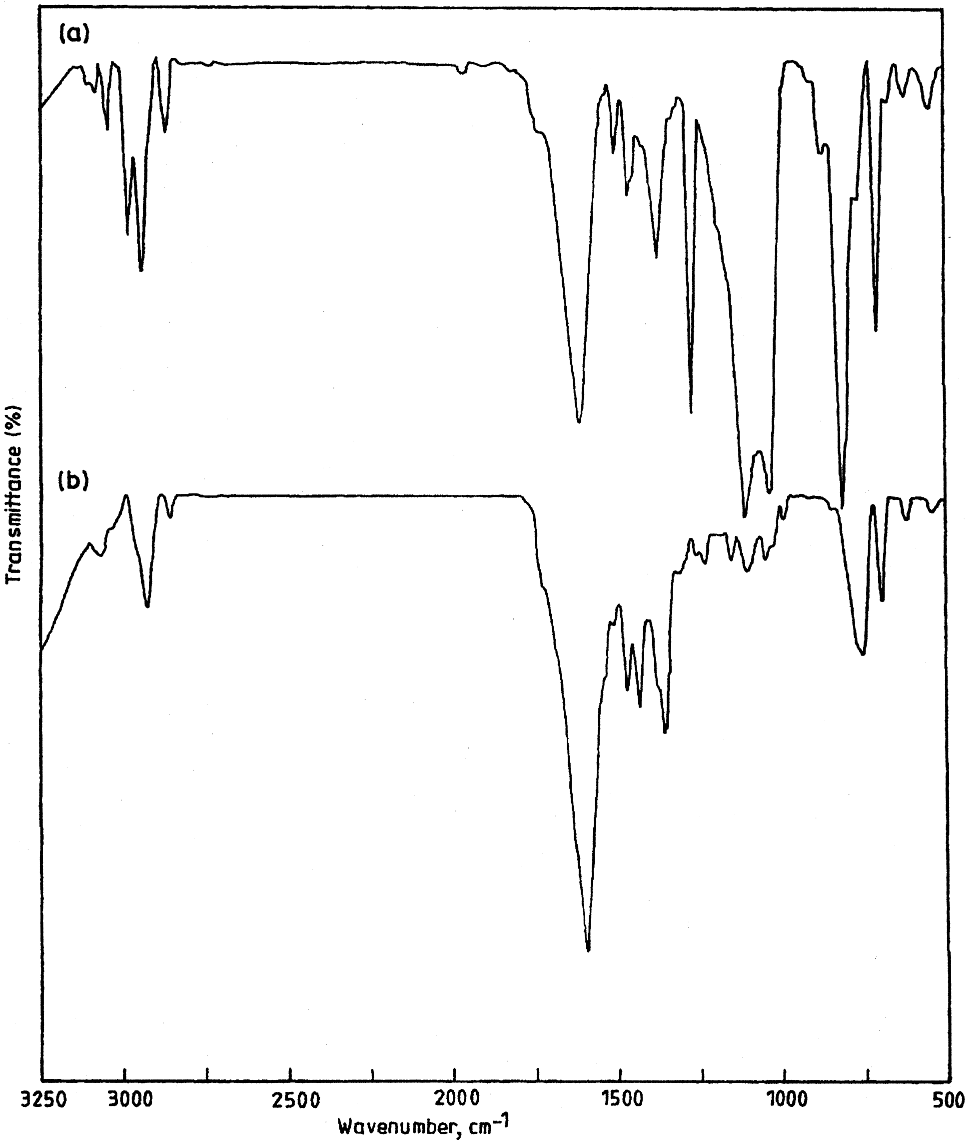


Figure 2. IR spectra of poly(styrene b-2-vinylpyridine) polymers shown in Table [M_n = 4853 as (a) and M_n = 19139 as (b)].

CONCLUSION

We have been able to prepare styrene-b-2-vinylpyridine copolymers of narrow molecular weight distribution by mechanism transfer from anionic to ATRP. The block copolymers are characterized by GPC, TLC, IR, and proton

NMR. This is the first report involving synthesis of poly(styrene-b-2-vinylpyridine) via mechanism transfer from anionic to ATRP.

ACKNOWLEDGEMENT

We wish to thank the Department of Science and Technology, India for the financial support (SP/S1/H28/95).

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Recevied November 15, 1999
Received received February 1, 2000