Polymer Bulletin 13, 109–114 (1985)

Polymer Bulletin

Towards the Synthesis of Electroactive Block Copolymers via Anionic-to-Ziegler-Natta Transformation Reactions

2. Evidence for the Formation of Styrene/Acetylene Diblock Copolymers

Mary E. Galvin* and Gary E. Wnek

Department of Materials Science and Engineering, Massachusetts Institute of Technology,
Cambridge, MA 02139, USA

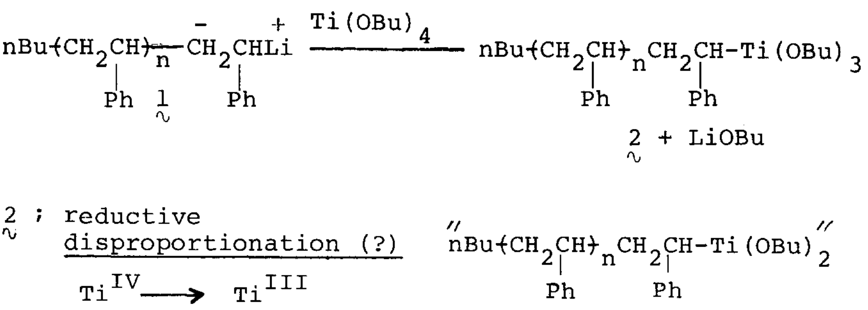
Summary

Diblock copolymers of acetylene and styrene were prepared by treating $Ti(OBu)_4$ with polystyryl lithium followed by reaction with acetylene. Reliable evidence for the formation of block copolymers was derived from dual radiotagging experiments.

Introduction

The intractability of polyacetylene has prompted the search for synthetic approaches which may render $(CH)_x$ soluble or at least processable as a particulate dispersion. We (1) and Baker and Bates (2) were the first to suggest and carry out the synthesis of block copolymers wherein one block was $(CH)_x$. The obvious motivation is that, if the second block has a great affinity for a particular solvent, the strong hydrophobic interactions (leading to crystallization) between $(CH)_x$ chains may be overcome affording solubility of the entire copolymer chain. Our methodology (Scheme I) involved the use of anionic-to-Ziegler-Natta transformation reactions (3, 4), a catalytically active titanium-based species being generated by alkylation of $Ti(OBu)_4$ with polystyryl lithium.

Scheme I

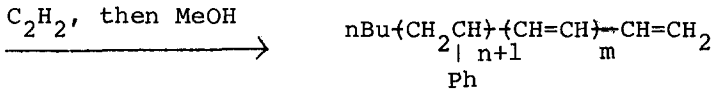


$$\underset{\underset{\sim}{1}}{nBu\!-\!(CH_2\underset{Ph}{CH})_n\!-\!CH_2\underset{Ph}{\overset{-}{CH}}\overset{+}{Li}} \xrightarrow{Ti(OBu)_4} \underset{\underset{\sim}{2}}{nBu\!-\!(CH_2\underset{Ph}{CH})_n CH_2\underset{Ph}{CH}\!-\!Ti(OBu)_3} + LiOBu$$

$$\underset{\sim}{2}\ ;\ \xrightarrow[Ti^{IV} \longrightarrow Ti^{III}]{\text{reductive disproportionation (?)}} \overset{//}{n}Bu\!-\!(CH_2\underset{Ph}{CH})_n CH_2\underset{Ph}{CH}\!-\!Ti(OBu)_2^{//}$$

---

* Present address: AT&T Bell Laboratories, Murray Hill, NJ 07974, USA



$$\xrightarrow{C_2H_2\text{, then MeOH}} \text{nBu}(CH_2\underset{\text{Ph}}{\underset{|}{CH}})_{n+1}(CH{=}CH)_m CH{=}CH_2$$

The anticipated success of this chemistry was predicated on the observations that Ti(OBu)$_4$/Li alkyl systems are active for acetylene polymerization (5), and electron donating ligands (such as -OBu, which donate e-density via resonance, a phenomenon similar to activation of a phenyl ring by -OH or -OR) tend to suppress β-hydride elimination (6), which can of course significantly lessen the yield of block copolymer. We report herein our recent studies which have been directed toward substantiating the ability of our synthetic approach to yield styrene-acetylene diblock copolymers.

Experimental

Block polymerizations were carried out in a reactor (7) consisting of a 500 ml round bottom flask to which directly was attached a Teflon stopcock and balljoint for connection to a vacuum line, a Teflon stopcock for introduction of Ar and, at the top of the flask, a graduated tube (100 ml cap.) via a Teflon stopcock. The flask was baked at 200°C *in vacuo* overnight and styrene (washed with aq. KOH and H_2O, dried over $MgSO_4$ and filtered, then dried over CaH_2) was distilled *in vacuo* into the graduated tube cooled to -196°C (with the reactor inverted). After warming to 25°C , 150 ml dry THF (distilled from Na benzophenone) was added to the flask under Ar. Next, the flask was cooled to -78°C and 0.3 ml nBuLi (2.1 ml in n-hexane) was added *via* a syringe under Ar. The THF/n-BuLi solution was degassed on a vacuum line and the stopcock to the styrene reservoir was opened gently and styrene was added over *ca.* 5 minutes. The flask was then removed from the -78°C bath and allowed to warm for 10 minutes. Next, 1 ml of Ti(OBu)$_4$ in dry toluene (0.21 M) was added to the polystyryl Li under Ar (Li/Ti = 3:1). Following 30 minutes of aging, the solution was degassed and *ca.* 1 atm C_2H_2 was admitted. The solution turned from red to green to deep blue as acetylene polymerization proceeded with blue-black particles developing at long reaction times. The $\bar{M}_n$ of polystyrene was typically limited to *ca.* 10,000 daltons to allow precipitation to occur, thus facilitating separation of block copolymer from unreacted polystyrene. Termination was accomplished by addition of 3 ml of 10% HCl in MeOH. Radio tagging studies were performed using ^{14}C-enriched BuLi (ICN; prepared from 2:1 nBuLi/^{14}C-nBuLi[ICN, 0.94 mCi/ml]) and CH_3OT (prepared from anhydrous CH_3OH and T_2O). Counting was done by New England Nuclear Corp.

Any precipitate was filtered, while "colored solutions" were separated from homopolystyrene by precipitation in 10% THF/90% acetone.

Results and Discussion

Several observations are consistent with block copolymer formation using our synthetic approach. First, no precipitate is noted early in the reaction, although the solution is deeply colored, suggesting true solubility. Second, the time required to afford precipitation of blue-black particles increased with increasing polystyrene length (15 min. for $\overline{M}_n$ = 32,000 and 36 min. for $\overline{M}_n$ = 42,000). Also, monitoring the composition of the precipitate as a function of increasing reaction time by IR spectroscopy showed (8) that indeed the $(CH)_x$ concentration increased. Unfortunately, the IR method cannot distinguish between block copolymer and a simple, physical mixture, whereas the other observations noted above are misleading as suggested by control experiments. For example, polymerization of C_2H_2 in the presence of polystyrene (freshly prepared by anionic polymerization and terminated with MeOH; this material should not contain electrophilic sites for grafting (2)) gave, with short reaction times, purplish "solutions" from which $(CH)_x$ particles could be precipitated by the addition of acetone. More significantly, the precipitate could be re-suspended in toluene, yielding what appeared to be a true solution. We believe that dissolved polystyrene may adsorb onto small $(CH)_x$ particles and prevent agglomeration under certain conditions. In fact, Edwards et al.(9) showed that $(CH)_x$ latices can be prepared by acetylene polymerization in the presence of appropriate dissolved polymers. These observations prompted us to search for formal proof of a covalent bond between polystyrene and $(CH)_x$.

Initial efforts focused on gel permeation chromatography (GPC), which demonstrated that indeed an increase in molecular weight was achieved (vs. initial polystyryl Li) upon acetylene polymerization (10). However, our materials were brominated prior to GPC analysis and chemistry might occur at this step (such as crosslinking) which could lead to a false interpretation of data. We decided that radio-labelling would provide a sensitive and thus highly useful indicator of block formation while allowing us to handle the materials in the pristine state. The idea behind the double labeling is simple. Polystyryl Li enriched with ^{14}C at the n-butyl terminus was used to alkylate $Ti(OBu)_4$, acetylene was polymerized until particulates precipitated, and finally, the polymerization was terminated with MeOT. The precipitate was washed exhaustively with toluene to remove homopolystyrene and then counted. A control reaction, in which ^{14}C-enriched polystyrl Li was terminated with CH_3OT to obtain a reference $^{14}C/T$ ratio, was also performed. If, in the block preparations, only homo $(CH)_x$ was formed due to facile β-hydride elimination (followed by initiation, via titanium hydrides), the precipitate should contain negligible $^{14}C/T$ (i.e. $^{14}C/T \sim 0$). If the residue was totally comprised of block copolymer, then the $^{14}C/T$ ratio should be similar to that of the control (assuming that kinetic isotope effects are similar; this is reasonable as typical values range between 2 and 3 (11)). Ratios of $^{14}C/T$ between the two extremes would provide information concerning chain transfer reactions.

Our preliminary results are summarized in Table 1. Clearly, all block copolymers [2-4] contain significant amounts of ^{14}C. That this is not derived to a significant extent from ^{14}C-labeled homopolystyrene which cannot be extracted is demonstrated by Sample #6. We believe the increase in $^{14}C/T$ observed in Samples 2-4 as the catalyst concentration increases may be due to be bimolecular termination mechanism, the occurrence of which is expected to increase with increasing catalyst concentration, viz.

$$2 \sim CH = CH-\overset{|}{\underset{|}{Ti}}- \rightarrow 2\ -\overset{|}{\underset{|}{Ti}} + \sim CH = CH_2 + \sim C \equiv CH$$

Thus, our preliminary data show no compelling evidence for the formation of any significant amount of homo-$(CH)_x$. Although the overall yield of block copolymers (defined as amt. block/amt. block + PS) is only ca. 2-5%, it appears that our materials are reasonably pure. While it may be argued that the low yield is the result of using THF as the solvent (which can compete with C_2H_2 in coordination with the active site), these numbers are not unreasonable for a soluble Ziegler-Natta catalyst.

We also note that the radio labeling approach allows an estimation of $\bar{M}_n$ of the $(CH)_x$ block. For example, for Sample 4 (Table 1), we find the $(CH)_x$ $\bar{M}_n$ to be ca. 30,000, whereas the polystyrene $\bar{M}_n$ was ca. 10,000 daltons. Clearly, the polystyrene block length is too short to render $(CH)_x$ chains of 30,000 daltons soluble. Future work will be directed toward characterization of styrene/acetylene diblock copolymers with particilar emphasis on the relationship between block length and electrical properties. Preliminary studies (7, 8) indicate that moderate conductivity upon I_2 oxidation (ca. 10^{-2} S/cm) is observed only in films of diblocks cast from solution which distinctly showed particulates. We have not as yet been able to render diblock films conductive ($\sigma < 10^{-6}$ S/cm) which were cast from "apparently soluble" (i.e., transparent blue-violet to the eye) systems.

Table 1

	sample	Li/Ti	[nBuLi],M	^{14}C, dpm/mg	T, dpm/mg	$\frac{^{14}C}{T}$
1.	Homopolystyrene	--	4×10^{-3}	9,226	22,256	0.46
2.	Block Copolymer A	3.8	2.6×10^{-3}	10,688	28,933	0.37
3.	Block Copolymer B	3.8	5.2×10^{-3}	14,266	24,358	0.59
4.	Block Copolymer C	3.0	8.7×10^{-3}	10,482	14,390	0.73
5.	Homopolystyrene from C	--	--	34,628	224	155
6.	Unlabeled block prepared in presence of ^{14}C, T-Containing homopolystyrene; extracted with toluene		8.7×10^{-3}	659	191	

Acknowledgements

The authors are grateful to the Office of Naval Research for generous support.

References

1. G.F. Dandreaux, M.E. Galvin and G.E. Wnek, Journal de Physique, Colloque C3, Supplement au n°6, Tome 44, C3-135 (1983).
2. F.S. Bates and G.L. Baker, Journal de Physique, Colloque C3, Supplement au n°6, Tome 44, C3-11 (1983).
3. D.H. Richards, The British Polymer Journal, 12, 89 (1980).
4. A. Siove and M. Fontanille, Makromol. Chem., 181, 1815 (1980).
5. W.H. Watson, Jr., W.C. McMordie, Jr., and L. Blands, Journal of Polymer Science, 55, 137 (1961).
6. G. Henrici-Olivé and S. Olivé, Chemtech, December, 746 (1981).
7. M.E. Galvin, Ph.D. Thesis, Massachusetts Institute of Technology (1984).
8. M.E. Galvin and G.E. Wnek, Polymer Preprints, 25(2), 229 (1984).
9. J. Edwards, R. Fischer and B. Vincent, Makromol. Chem., Rapid Commun., 4, 393 (1983).

10. M.E. Galvin and G.E. Wnek, Polymer Preprints, 24(2), 14(1983).
11. N.R. Johnson, E. Eichler and G.D. O'Kelley, "Nuclear Chemistry, Technique of Inorganic Chemistry," vol. 2, Interscience, New York, p. 74 (1967).

Accepted February 5, 1985