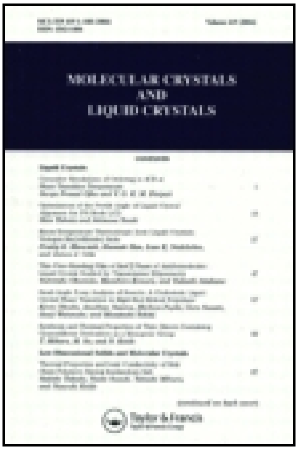

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Block Copolymers Containing Polyacetylene Units

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BLOCK COPOLYMERS CONTAINING POLYACETYLENE UNITS

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Abstract Styrene-acetylene block copolymers were prepared by an anionic to Ziegler-Natta transformation technique. Dual radio-active labelling was used to confirm the synthesis of block copolymers.

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 between $(CH)_x$ chains may be overcome leading to solubility of the entire copolymer chain. Our methodology 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. 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 ring by -OH or -OR) tend to suppress B-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 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 -200° 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*. 1atm C_2H_2 was admitted. The solution turned from red to green to deep blue as acetylene polymerization proceeded. Termination was accomplished by addition of 3 ml of 10% HCl in MeOH. Radio tagging studies were performed using ^{14}C-enriched in BuLi (ICN) and CH_3OT (prepared from 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 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 precipiated by 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. [7] 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. 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 polystyryl 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). 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 occurrance of which is expected to increase with increasing catalyst concentration.

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

Thus, our preliminary data show no compelling evidence for the formation of any significant amount of homo $(CH)_x$. Although the overall yeild 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. Future work will be devoted to characterization of the copolymers in terms of microphase separation and the general dependence of block length and concentration on electrical properties.

Table 1

	sample	Li/Ti	[nBuli] M	^{14}C, dpm/mg	T, dpm/mg	$\frac{^{14}C}{T}$
1.	Homopolystyrene	--	?	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 tolvene	3.0	8.7×10^{-3}	659	191	

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