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SYNTHESIS OF GRAFT AND BLOCK COPOLYMERS CONTAINING (CH)$_x$ SEGMENTS

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I - INTRODUCTION

Copolymerization has traditionally been a fruitful approach for the construction of organic materials possessing specific chemical, physical and mechanical properties. Copolymers are classified as random, alternating, graft or block depending upon the structural arrangement of the comonomer units. Random (or nearly so) copolymers of acetylene and methylacetylene have been prepared/1/ which exhibit, as expected, electrical conductivities upon doping which are highly dependent upon comonomer concentration. The decrease in conductivity with increasing methylacetylene concentration has been rationalized/1,2/ as being due to disruption of planarity of the backbone. A similar argument apparently applies to the acetylene/phenylacetylene system/3/. Interest has developed in this laboratory concerning the possibility of attaching a wide variety of polymer chains to the (CH)$_x$ backbone (i.e., grafting). A motivation for such work is the possibility of tailoring the surface properties of (CH)$_x$ for electrode applications. The ability of alkali metal graphitides/4/ to initiate polymerization of several monomers suggested the use of doped (CH)$_x$ in this capacity with the prospect of covalently binding polymer chains to (CH)$_x$ backbones. Block copolymers are also of interest because the planarity of the (CH)$_x$ block is expected to remain essentially intact, allowing the electrical properties to be primarily determined by percolation of (CH)$_x$ domains. Furthermore, soluble and tractable derivatives could be envisioned by judicious choice of the remaining block(s). Acetylene polymerization will necessarily be initiated by coordination catalysts. We have considered the possibility of using the "alternate feed" method to produce, for example, ethylene-acetylene block copolymers from appropriate transition metal catalysts. However, such catalytic systems are typically not suitable for the synthesis of well-defined blocks/5/ due to variable initiation rates of the catalytic centers and undesirable termination reactions. The exploitation of active polymer-transition metal bonds for the synthesis of block copolymers/6,7/ suggested a potentially viable approach. Specifically, we have attempted to use "living" polystyrene to alkylate Ti(0Bu)$_4$ followed by acetylene polymerization, viz
A potential advantage of such a transformation reaction /7/ is that at least the first block (polystyrene) can be synthesized with a well-defined chain length. Preliminary experiments and observations are presented in this article.

II - EXPERIMENTAL

Polyacetylene films were synthesized at -78°C using techniques similar to those developed by Shirakawa and coworkers /8/. Reductive doping was carried out in a dry box by immersion of (CH)x films in 1 M sodium naphthalide/TiF solutions for 2 min. The films were then washed several times with dry, O2-free TiF and allowed to stand in fresh THF for approximately 1 hour. The conductivities and compositions of the films were in the range 5-50 S/cm and [CHNa0.20-0.25]x, respectively.

Exposure of the n-type films to either liquid (styrene, methyl methacrylate) or gaseous (ethylene oxide, isoprene) monomers resulted in polymerization. Much of our initial work has focused on grafting of poly(ethylene oxide) (PEO) to (CH)x in an effort to render the (CH)x surface more hydrophilic and to provide covalent attachment of a material capable of functioning as a solid electrolyte /9/. Films of n-type (CH)x were exposed to dry (CaH2-treated), gaseous ethylene oxide in the range 55-75°C with initial pressures being ca. 500 torr. Reaction times were typically 5 hours. The films were washed with dry, O2-free methylene chloride to remove non-covalently bound PEO and then with deaerated H2O to protonate oxyanions and remove the NaOH byproduct. The presence of bound PEO after extraction was confirmed by IR spectroscopy.

The synthesis of block copolymers were attempted in the following manner. "Living" polystyrene was first prepared by conventional anionic techniques using n-BuLi as the initiator in THF at -78°C. (The appropriate styrene/n-BuLi ration was employed to afford an Mn of approximately 10,000 for the polystyrene block). In initial experiments, this polystyryl lithium product was treated with AICl3 to afford a polystyryl Al species which could be capable of alkylating Ti(0Bu)4. However, we find it to be more useful to directly alkylate Ti(0Bu)4 with the polystyryl Li. The orange-red polystyryl Li solution became deep red upon treatment with Ti(0Bu)4 at -78°C (Li/Ti = 2:1). The solution was warmed to room temperature and dry, O2-free acetylene (initial pressures ca. 700 torr) was introduced on a vaccum line. The solution became deep blue in color and after approximately 30 min. fine blue-black particulates were observed. The polymerizations were terminated by addition of MeOH. The precipitated polymers were extracted with THF for 6 hours.

III - RESULTS AND DISCUSSION

The primary reaction of n-type (CH)x and ethylene oxide is presumably attack of a carbanion on a methylene carbon resulting in ring opening and oxyanion formation, followed by successive monomer additions:
The fact that approximately half of the product can be removed by CH$_2$C$_1$2 extraction may suggest that electron transfer from a (CH)$_x$ radical anion to ethylene oxide occurs leading to polymerization without attachment to the (CH)$_x$ or that some attached PEO suffered mechanically-induced scission. The oily character of the extracted PEO suggests a low molecular weight. We have no information regarding the molecular weight of the covalently bound PEO or the number of PEO branches. The (CH)$_x$/PEO materials can be doped with I$_2$ to afford conductivities of approximately 10$^{-4}$ cm$^{-1}$. Problems with electrical contacts due to an insulating PEO layer may be a factor in this lower conductivity compared with I$_2$-doped (CH)$_x$ but it should be noted that the (CH)$_x$ conjugation is broken at the graft points and this is expected to reduce the intrachain hole mobility. More detailed characterization of these materials is in progress.

The work on block copolymers is very recent and therefore little definitive information is available. A crucial point is of course a formal proof of block copolymer formation and at this time we have no conclusive evidence. However, the transformation approach has been demonstrated to be effective in the synthesis of block copolymers and there is no reason why a priori the chemistry described in the experimental section is not feasible. It is worth noting that extraction of a presumed block copolymer having a polystyrene/(CH)$_x$ ratio of ca. 10:1 (based on the amount of polystyrene in the reaction vessel and molar uptake of acetylene during subsequent polymerization) removes approximately 40 wt.% of material which is homopolystyrene. The remainder may be polystyrene attached to (CH)$_x$ blocks, the latter being aggregated into crystalline domains which are insoluble. Doping of the material with I$_2$ affords a conductivity of $<10^{-8}$ S/cm and our feeling is that probably an insulating polystyrene layer prevented the formation of good electrical contacts. The efficiency of the block copolymerization chemistry, proof of block formation and, ultimately, the influence of microphase separation on electrical properties are the subjects of future study. The observation of transparent blue solutions in the early stages of the acetylene polymerizations is particularly interesting.

IV - ACKNOWLEDGEMENTS

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V - REFERENCES