

Dedicated to Professor Ionel Haiduc
on the occasion of his 70th anniversary

SELF-ASSEMBLY OF FUNCTIONAL POLYMERS. A VISCOMETRIC STUDY

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Received February 9, 2007

The paper outlines the design of well defined polystyrene and polyisoprene functionalized with dibenzo-24-crown-8 and secondary ammonium end groups, respectively. Viscosity measurements were used to evidence the formation of supramolecular assemblies through the connection of these building blocks by mutually interacting moieties.

INTRODUCTION

Supramolecular chemistry has been developed intensively in the last decades as a new line of research and much attention has been directed towards the synthesis of new supramolecular assemblies composed of groups of molecules linked together through non-covalent molecular interactions. Their preparation is based on the molecular recognition principle – one component being the host and the other acting as a guest – and is influenced by the cooperation of various non-covalent interactions. Cyclic molecules play the role of hosts while the role of *guests* is played by a wide range of small molecules or various polymers.¹⁻³

The application of the principles of macromolecular recognition is used to design self assemblies of chemically different building blocks into supramolecular structures. The complexation of cyclic species linked to a polymer sequence with suitable complementary polymeric guests is aimed to control the sizes and shapes of the resultant polymolecular aggregates in solution as well as in the solid state. Additionally, a great advantage of this modular approach is given by the fact that 3D block copolymer objects can be obtained avoiding difficult synthetic steps. The new proposed systems have the potential to broaden the scope of structures and processes useful in the self assembly of pseudorotaxanes, and also to increase the thermodynamic driving forces for threading, a key

to an increased efficiency and control of the process.

The self-assembling functionalization of polymers usually requires high-affinity binding recognition motifs between the components. One example of such high affinity binding recognition is the complexation between alkylammonium ion centers and crown ether units, e.g. dibenzo-24-crown-8 (DB24C8) linked to polymer chains.^{4,7} The mixing of such components in 1:1 molar ratio results in the formation of a pseudorotaxane complex held by strong hydrogen bonds between the acidic NH_2^+ protons and the oxygen atoms in DB24C8 ring.

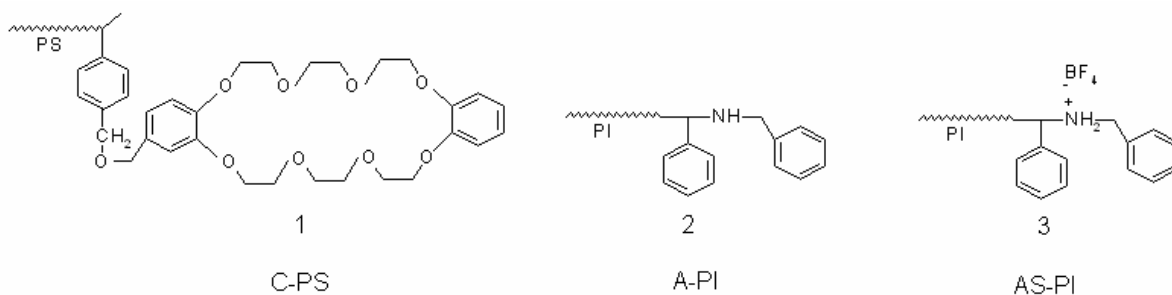
Our efforts have recently focused on the use of pseudorotaxane self-assembly to build noncovalent block copolymers.^{2,3} This method complements hydrogen bond-driven associations that do not form chemical linkages but have been proved to be effective in producing supramolecular polymers.⁸ The paper deals with the viscometric evidence of the self assembly of styrene and isoprene oligomers functionalized with DB24C8 and dibenzylammonium tetrafluoroborate, respectively.

RESULTS AND DISCUSSION

The functional precursors, crown ether functionalized polystyrene (C-PS) and dibenzylamine terminated polyisoprene (A-PI), with the structures presented in Scheme 1, were prepared by two different, well controlled techniques. A-PI was

prepared by anionic polymerization of isoprene initiated by *sec*-butyllithium and stopping the chain growth by sequentially adding *N*-benzylidenebenzylamine and methanol, according to a method proposed by Quirk,⁹ while, to prepare C-PS, the free radical polymerization of styrene was performed in the presence of a TEMPO initiator containing DB24C8 units, according to a

procedure described by Gibson.¹⁰ A-PI was further neutralized with tetrafluoroboric acid to obtain dibenzylammonium tetrafluoroborate terminated polyisoprene (AS-PI). The molecular weights and the polydispersity indexes of the obtained polymers are as follows: C-PS: $M_n = 4\ 000$ g/mol, $M_w/M_n = 1.42$; A-PI: $M_n = 6\ 800$, $M_w/M_n = 1.28$.



Scheme 1 – Structure of polymer precursors functionalized with mutually interacting groups.

The self-assembly of the functionalized precursors takes place through the complexation of the end groups of polyisoprene (guest) by the crown ether moieties in C-PS (host).

One of the simplest and widely used tests for the estimation of interactions in mixed polymer solutions is the measurement of mixture intrinsic viscosity *versus* its composition. The experimental values of mixture intrinsic viscosity have to be then compared with the calculated additive curve, which ignores the interactions between the components. Any deviations of experimental results from the additive value would indicate the presence of specific interactions between the two polymers.¹¹⁻¹⁶

In our study, the intrinsic viscosities $[\eta]_{\text{C-PS}}$ and $[\eta]_{\text{A-PI or AS-PI}}$ were measured as limit to zero concentration of the reduced viscosity (Figure 1). The additive values of the intrinsic viscosities of solution mixtures having 1:1 molar ratios between mutually interacting groups were calculated with the formula $[\eta]_{\text{add mix}} = W_{\text{C-PS}}[\eta]_{\text{C-PS}} + W_{\text{A-PI or AS-PI}}[\eta]_{\text{A-PI or AS-PI}}$ (where $W_{\text{C-PS}}$ and $W_{\text{A-PI or AS-PI}}$ are the weight fractions of each component in the mixture; $W_{\text{C-PS}} = 0.33$ and $W_{\text{A-PI or AS-PI}} = 0.67$). The calculated values of the additive intrinsic viscosities are compared with the experimental ones in Table 1.

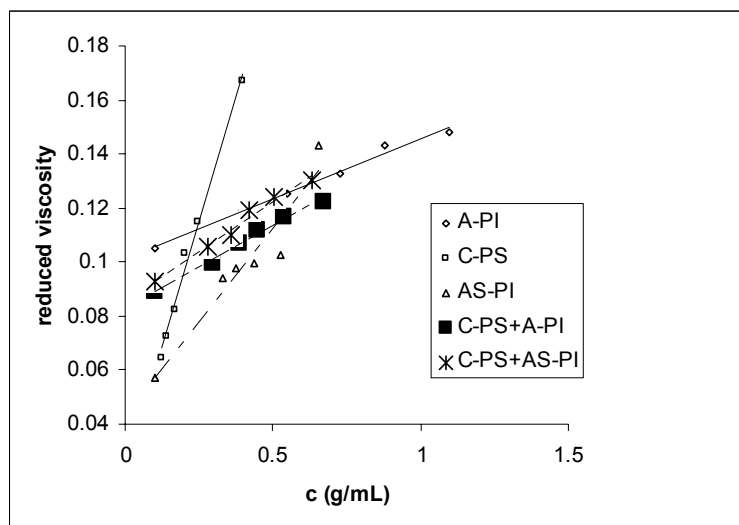


Fig. 1 – Reduced viscosity *versus* concentration for functional polymers and for their mixtures.

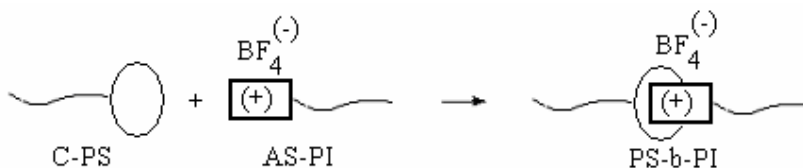
Table 1

Intrinsic viscosity values of functional polymers and of their mixtures

Cod	Experimental intrinsic viscosity $[\eta]$ (L/mol)	Calculated intrinsic viscosity $[\eta]_{\text{add mix}}$ (L/mol)
C-PS	0.013	
C-PS + A-PI	0.074	0.073
A-PI	0.102	
AS-PI	0.043	
C-PS+AS-PI	0.089	0.033

As one can see from the values in Table 1, the functional prepolymers, C-PS and A-PI, in chloroform solutions, show one order difference in their intrinsic viscosity values, according to their molecular weights. The 1:1 mixture of these functional polymers shows an intrinsic viscosity close to the additive value, indicating the formation of a physical mixture (no interaction or a poor interaction with a rapid change between the complexed and non complexed structures). Contrary to this system, the 1:1 mixture between C-PS and AS-PI (the salt functionalized PI) presents a higher intrinsic viscosity as compared to

the additive value, denoting the formation of a higher molecular weight compound, i.e. the block copolymer with the structure depicted in Scheme 2. The block copolymer results through the complexation between the crown ether and ammonium salt end functionalities of the prepolymers. The difference in interacting activities of AS-PI and A-PI with C-PS supports the already known finding, *i.e.*, a stronger interaction is exhibited in ammonium salts/crown ethers systems as compared to that shown by amines/crown ethers systems.^{18,19}



Scheme 2 – Schematic representation of the preparation of the self-assembled block copolymer.

EXPERIMENTAL PART

Synthesis of polyisoprene functionalized with secondary ammonium salt groups (AS-PI)

AS-PI was obtained by anionic polymerization of isoprene, according to a procedure proposed by Quirk et al.⁹ *Sec*-butyllithium (8.46 ml, 11 mmol) was added under positive N₂ flow to a 3-neck flask containing 200 ml of cyclohexane, 28 ml triethylamine and isoprene (32 ml, 323 mmol). The obtained white-yellow solution was stirred for 12 hours at room temperature under N₂ protection and 1.5 equivalents of *N*-benzylidenebenzylamine (3.22 g, 16.497 mmol) in 5 ml cyclohexane were then added. The reaction mixture was kept at room temperature for additional 48 h before quenching with methanol (3 ml) and stabilizing with 2,6-di-*tert*-butyl-4-methylphenol (BHT) (0.2 g, 0.1 wt. %). A-PI was recovered as a white-yellow rubber (21.2 g, yield 96.4 %) by precipitation in a large amount of methanol and was purified by reprecipitation from chloroform/methanol system and drying under vacuum for 24 h.

¹H-NMR, CDCl₃: new peaks at $\delta = 3.4$ ppm and 7.26 ppm attributed Ph-NHR and Ph groups.

¹³C-NMR, CDCl₃: new peaks at $\delta = 39.8, 49.8, 50.3, 67.6, 68.1, 127.9$ and 132.8, not observed in the ¹³C-NMR spectrum of the non functionalized polystyrene.

IR (KBr pellets): very small peak at 3314 cm⁻¹ attributed to secondary amine group.

The content of the amine chain end-groups in A-PI was determined by titration of a A-PI solution in 1/1 (v/v) chloroform/glacial acetic acid mixture with 0.103 N perchloric acid in glacial acetic acid, in the presence of methyl violet base indicator.

Synthesis of polystyrene functionalized with 24-crown ether end groups (C-PS)

C-PS was prepared according to the method of Gibson et al.¹⁰ The synthetic approach will be reported elsewhere.

Functionalized polyisoprene analyses

Characterization methods

The molecular weights were determined by gel permeation chromatography (GPC) using a Polymer Laboratories (PL-EMD 950) instrument equipped with an evaporative mass detector; polystyrene standards were used for calibration and toluene as a solvent.

The viscosity measurements were carried out using a conventional Ubbelohde viscometer that was placed in a thermostatically controlled bath with a precision of 0.01 °C. Measurements were initiated after about 15 min equilibration

time. The flow times were determined from an average of several readings (five readings). To obtain the mixtures of 1:1 molar ratio between mutually interacting end groups, the host and guest polymers were accurately weighed separately into volumetric flasks and diluted with solvent and aliquots of these solutions were mixed.

CONCLUSIONS

Polymers functionalized with crown ether and ammonium salt mutually interacting groups offer a protocol for reversible formation of pseudorotaxane-type block copolymers (complexation of the polymer functionalized with ammonium salt groups and the decomposition of the complex when the salt group is transformed into amine units in a basic medium). We are actively studying these approaches and the resulting novel materials.

ACKNOWLEDGEMENTS. The authors are grateful to the Romanian Ministry of Education and Research for financial support (CNCSIS GR 308/2006 and CEEEX 40(510)). One of the authors (A. Farcaş) would also like to thank Prof. H. W. Gibson from Virginia Tech., Department of Chemistry, USA for the opportunity to work in supramolecular chemistry under his guidance.

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