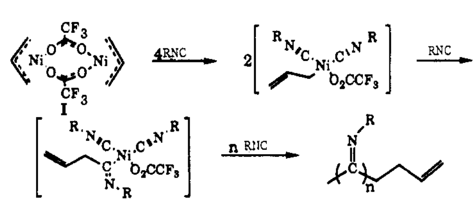
"Change of Mechanism" Block Copolymerizations. Formation of Block Copolymers Containing Helical Polyisocyanide and Elastomeric Polybutadiene Segments

Tayloring polymers for specialized applications often requires the synthesis of block copolymers that offer a combination of properties unobtainable from simple polymer blends or random copolymers.[1] Homopolymers with vastly different properties may be combined to create block copolymers that retain the often dissimilar properties of their components (e.g., hydrophilic and hydrophobic segments) yet are in fact single, homogeneous materials. Although block copolymers usually do exhibit a phase-separated morphology, it is on a much smaller scale than the separation obtained by using polymer blends. The small domain size and excellent interphase adhesion resulting from the microphase morphology can produce a high degree of transparency and exceptional mechanical properties.[1]

It must be emphasized that a high degree of structural control is essential in order to achieve the ultimate properties inherent in such two-phase materials. For this reason, living polymerization techniques are often the method of choice for block copolymer synthesis.[2] Unfortunately, transition-metal-catalyzed living polymerizations involving C–C bond formation are fairly rare and limited to a small monomer selection, which leads to an even smaller selection of block copolymers that can be easily prepared.[3] We report herein the application of a recently developed living polymerization system toward the synthesis of polybutadiene–polyisocyanide block copolymers which cannot be synthesized through either cationic, anionic, free radical, or other transition-metal-mediated techniques.[4]

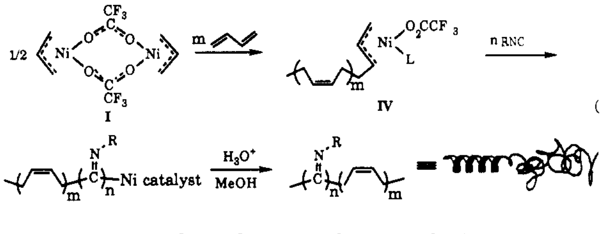
During our investigations into the development of an active, homogeneous catalyst for isocyanide polymerizations, we have discovered the compound $[(\eta^3\text{-}C_3H_5)\text{-}Ni(OC(O)CF_3)]_2$ (I) to be very effective in this regard. Compound I is able to quantitatively polymerize sterically bulky *tert*-butyl isocyanide (II) to the corresponding helical polymer[5] and also catalyzes the "living" polymerization of less hindered monomers (e.g., α-methylbenzyl isocyanide (III); eq 1).[6] In addition, I has previously received attention as a catalyst for the living polymerization of butadiene to yield >98% pure *cis*-1,4-polybutadiene.[7]



(1)

We have utilized the versatility in catalyst I to prepare, through a "change of mechanism" polymerization, novel block copolymers containing polyisocyanide and polybutadiene segments. The abundant functionality present in these copolymers (olefins and imines) potentially makes them "parent" block copolymers, which, through standard organic reactions, can be manipulated into a wide variety of "derivative" copolymers with entirely different properties.[8] In addition, the crystallinity and rodlike helical character of the polyisocyanide chains combined with the elastic properties of the polybutadiene segments make this block copolymerization technology a candidate for the preparation of a new class of thermoplastic elastomeric materials.[9]

It has been proposed that the living polymerization of butadiene mediated by I propagates via an η^3-allylnickel trifluoroacetate species (IV) with the polymer chain bound to one end of the allyl group.[7] We note that this active propagating species IV is identical to I with respect to the catalysis of living isocyanide polymerizations (i.e., both contain a nucleophile (allyl group) and an electron-withdrawing group). Therefore, the polymerization of isocyanides using active nickel catalysts derived from butadiene polymerizations with I, as described above, should afford butadiene/isocyanide block copolymers (eq 2).



(2)

Treatment of butadiene with a catalytic amount of I followed by subsequent treatment of the reaction mixture with either II or III afforded the block copolymers. GPC analysis of these materials showed unimodal distributions, confirming their copolymeric nature, and gave molecular weights that varied with monomer concentrations (Table I) and polydispersities that ranged from 1.7 to 2.4.[10] The lack of any homopolymer (polybutadiene) in the GPC traces indicated that all chain ends were converted to active isocyanide polymerizations. Furthermore, successful complete extraction of the copolymeric products into *n*-heptane (a solvent for polybutadiene and a nonsolvent for poly-III) confirmed the lack of contamination of the products by polyisocyanide homopolymer. This agrees well with our previous work where we showed that isocyanide polymerizations with I underwent quantitative initiation of all the catalyst centers.[6] Differential scanning calorimetry (DSC) performed on selected block copolymers showed glass transitions (T_g's) = −93 °C, which corresponded well with T_g's = −95 °C measured for pure polybutadiene (~75% cis) prepared using I under identical reaction conditions. These DSC results show[11] that significant butadiene chains (blocks) exist in these copolymers as opposed to small, random segments. The blocklike nature of these copolymers was also confirmed by use of $^{13}C\{^1H\}$ NMR spectroscopy. $^{13}C\{^1H\}$ NMR showed only resonances for the parent homopolymers and none was detectable that could be assigned to butadiene/isocyanide copolymer linkages, indicating these were few in number.

The microphase morphology of these block copolymers was investigated by using scanning electron microscopy (SEM). Micrographs of spin-cast thin films of the parent homopolymers (namely, pure polybutadiene and pure polyisocyanide) lacked significant surface features, consistent with expectations for homogeneous, single-phase materials. However, micrographs of transparent, thin films of the polyisocyanide/polybutadiene block copolymers showed highly textured morphologies distinctly characteristic[1] of microphase separations (Figure 1). In this example, the polyisocyanide (minor) component apparently exists as spherical or cylindrical domains dispersed in a continuous polybutadiene (major component) phase. From the micrograph, the polyisocyanide domain sizes can be estimated to be on the order of ~0.2 μm in diameter.[12] Cylindrical or spherical domains dispersed throughout a continuous

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Table I

polymn syst	I, μmol	diene, mmol	RNC, mmol	$\bar{M}_n$ (PBD)[a]	PDI[b] (PBD)[a]	$\bar{M}_n$ (block)[c]	PDI[b] (block)[c]	yield,[d] %
butadiene/II	17	5.2	2.7	8 070	1.64	9 900	1.71	94
butadiene/IIIA	5.6	3.6	5.5	50 300	1.67	120 900	2.36	84
butadiene/IIIB	5.6	7.2	3.6	77 700	1.73	126 300	1.98	92
butadiene/IIIC	5.6	11	1.8	129 800	2.10	152 500	2.29	85

[a] PBD = polybutadiene; $\bar{M}_n$ is of a small aliquot of this polymer before addition of isocyanide monomer. [b] PDI = polydispersity index, as determined by GPC = $\bar{M}_w/\bar{M}_n$. [c] $\bar{M}_n$ is of the total copolymer product. [d] Total isolated yield of block copolymer.

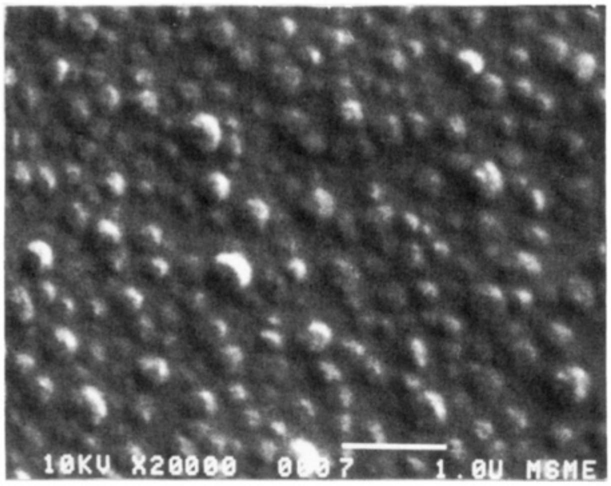

Figure 1. Poly(methylbenzyl isocyanide) ($\bar{M}_n$ = 40 000)/polybutadiene ($\bar{M}_n$ = 100 000) (30%/70%) block copolymer.

phase are typical for A–B block copolymers of similar composition,[1] and our observance of these domains supports the blocklike nature of our copolymers.

These results supported our expectations about the block copolymers, namely, that randomness or tapering of monomer components along the backbone would be minimal, if not negligible. Our hypothesis came from the realization that, upon switching monomer to isocyanide, the catalyst undergoes such drastic changes that the subsequent incorporation of butadiene units is unfeasible. We have shown this by a "reverse block" experiment where we were unable to polymerize butadiene *after* polymerizing isocyanide with I.

The reasons for this are many. First, isocyanides are very high field ligands and form much stronger bonds with nickel than does butadiene.[13] Thus, butadiene is unable to compete with isocyanides for coordination positions on the nickel catalyst centers and hence cannot be polymerized under these conditions.[14] Second, we have shown[6] that the catalyst is in fact reduced to a nickel(I) species by isocyanide under polymerization conditions. Butadiene polymerizations via nickel have been shown to be extremely sensitive to the Lewis acidity of the metal center,[7] and so, while nickel(I) does polymerize isocyanides, the less acidic nickel(I) center would not be expected to efficiently polymerize butadiene. Finally, polymerization of isocyanide after butadiene fundamentally involves the insertion of isocyanide into an allylic nickel–carbon bond, a reaction with precedent.[15] On the other hand, polymerization of butadiene after isocyanide involves insertion of butadiene into an iminoacyl nickel–carbon bond, a reaction that, to our knowledge, has not been observed.

In summary, these block copolymerizations represent a departure from conventional metal-catalyzed block copolymerization systems. This system is unusual in that it employs one metal to very efficiently polymerize two very different monomers, a scenario seldom encountered. In addition, the two polymerizations proceed via different mechanisms and even with the catalyst in different oxidation states. Furthermore, the extreme dissimilarity between isocyanide and butadiene polymerizations permits, even requires, sharp block junctions with negligible tapering, giving very well-defined materials.

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Supplementary Material Available: Experimental procedures for the polymerizations and spectral and characterizational techniques (2 pages). Ordering information is given on any current masthead page.

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(10) These relatively broad molecular weight distributions are due primarily to the butadiene polymerization step of the synthesis and are consistent with earlier findings.[7] Additional broadening due to the polyisocyanide segments (see Table I) is due to the use of racemic III instead of the pure enantiomers (i.e., a homopolymerization of racemic III will generally have a PDI ≈ 1.5–1.7, while a homopolymerization of either (*R*)- or (*S*)-III will have a PDI ≈ 1.1–1.2). This behavior was found to be due to stereoselection effects in polymerizations of chiral isocyanides, which we plan to report in a future publication.[6c]

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(12) A reviewer has noted that microdomains of this size are atypically large for a polymer of this molecular weight ($\bar{M}_n$ = 40 000). We feel these large microdomains might possibly be due to the rigidity of isocyanide polymers as well as the relative broadness of the molecular weight distributions in these samples.[4]

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