Pseudo-tetrablock copolymers with ethylene and a functionalized comonomer

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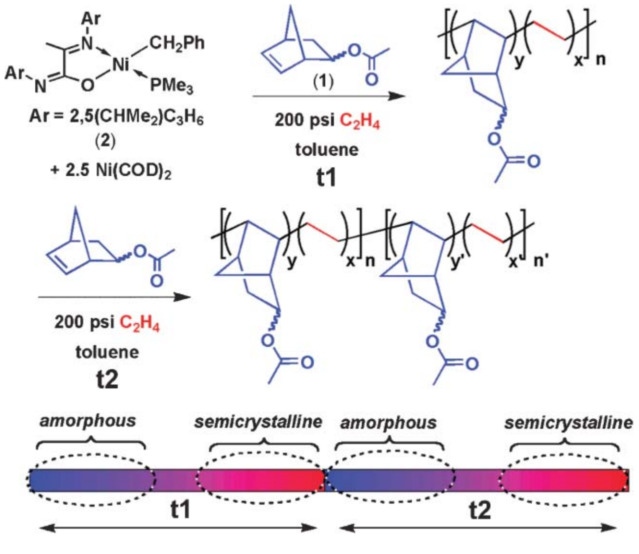
Pseudo-tetrablock copolymers comprised of ethylene and 5-norbornen-2-yl acetate (1), were synthesized using the initiator system (L^iPr_2)Ni(η^1-CH_2Ph)(PMe_3) (2) [(L^iPr_2) = *N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamide] and 2.5 equivalents of $Ni(COD)_2$ [bis(1,5-cyclooctadiene) nickel.

Polymer structures with higher-level architectures, such as block-, multiblock- and tapered copolymers are important for achieving properties not available with linear homopolymers.[1] Controlled polymerization reactions are necessary for achieving these structures,[2] which are a particular challenge for ethylene and functionalized co-monomers.[3,4] Multi-block copolymers that possess soft amorphous regions bound at either end by hard, crystalline segments find much utility as thermoplastic elastomers. The soft component provides for elastomeric properties, while the crystalline phase acts to anchor the chains in place. An often-quoted requirement is that the blocks should have sufficiently different Flory–Huggins interaction parameters, *i.e.* be immiscible with each other, such that phase separation takes place.[5]

We recently reported the quasi-living polymerization of C_2H_4 and 5-norbornen-2-yl acetate (**1**) using an initiator system generated from (L^iPr_2)Ni(η^1-CH_2Ph)(PMe_3) (**2**) (L^iPr_2 = *N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)propanamide)[6] and 2.5 equiv. $Ni(COD)_2$ (bis(1,5-cyclooctadiene)nickel).[4] It is possible by a pressure-jump technique to synthesize block-copolymers containing segments with different ratios of C_2H_4 and **1**.[7] Tapered copolymers (TCPs) have also been prepared with this initiator system by a single batch method that allows depletion of **1** under a constant ethylene pressure.[8] It was observed that the tapering profile depends on the initial concentration of **1**, with the highest initial fractional content of **1** in the chain corresponding to the highest initial concentration of **1** in the reaction medium. Semicrystalline properties are observed after specific reaction times, consistent with the fact that C_2H_4-rich segments are produced as **1** depletes. In addition, the ratios of **1** to C_2H_4 on the termini of each chain are sufficiently different that microphase separation is obtained.

Based on the two copolymerization procedures described above, it seemed reasonable that polymer chains that resembled tetrablock-type structures could be prepared by the process shown in Scheme 1. One begins the polymerization with a set concentration of **1** under a constant C_2H_4 pressure. The reaction is allowed to continue for a time t_1, during which [**1**] decreases in the reaction medium, leading to an increase of C_2H_4 incorporation relative to **1**. After completion of t_1, a second batch of **1** is added to the reactor, such that [**1**] is re-established to that at the beginning of the reaction. The reaction is then allowed to proceed for a time t_2. The amount of **1** to be added at t_1 is determined by stopping a TCP polymerization at t_1, determining the molar incorporation of **1** in the resultant TCP and from this and the polymer yield determining the amount of **1** that was consumed in t_1. The addition of more monomer at t_1 results in a sudden increase in the incorporation of **1**, followed by a depletion process similar to that expected during t_1. The end result is a backbone containing two similar TCP structures covalently joined in a head to tail fashion. The idea is schematically illustrated in Scheme 1, where the ratio of **1** (blue) to C_2H_4 (red) in the chain tapers to a point where the C_2H_4 content is sufficiently high that a semicrystalline segment is obtained. Each TCP segment provides for an amorphous and a semicrystalline component. Thus, each chain contains four distinct regions, similar to a tetrablock copolymer.

A series of copolymerization reactions designed to test the feasibility of Scheme 1 is summarized in Table 1. We focused on reactions where t_1 = t_2 to keep the dimensions of the two tapered segments as similar to each other as possible. Examination of the



Scheme 1 Synthesis of pseudo-tetrablock copolymers.

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Table 1 Summary of polymerization reactions

	t_1[b]	t_2[b]	*Mn*[c]	PDI	Mol% **1**[d]	T_m[e,f]	X_C[f]	T_g[e,g]
1	30	30	95	1.4	14	63	0.09	16
2	45	45	156	1.4	9	67	0.09	15
3	55	55	168	1.6	6	102	0.15	17
4	60	60	181	1.4	7	97	0.17	13
5	60	60	202	1.4	8	100	0.19	17

[a] Conditions: P_{C2H4} = 200 psi, [**1**]$_0$ = 0.15 M, [**2**] = 0.67 mM, [Ni(COD)$_2$] = 1.67 mM, in toluene. [b] minutes. [c] kg mol^{-1}, by using gel-permeation chromatography. [d] ^{1}H NMR spectroscopy in 1 : 4 C_6D_6–1,2,4-trichlorobenzene. [e] °C. [f] Differential scanning calorimetry. [g] Dynamic mechanical analysis (tan δ_{max}).

trends in Table 1 shows that *Mn* increases with the total reaction time ($t_1 + t_2$). Indeed, doubling the reaction time increases *Mn* by a factor close to two (entry 1 *vs.* entries 4 and 5). The polydispersity index of the polymers is contained between 1.3 and 1.6, as previously observed for TCPs obtained *via* this reaction process. ^{1}H NMR spectroscopy shows that the total content of **1** decreases with increasing reaction time (entries 1–5). DSC measurements show melting transitions (T_m) between 63 °C and 102 °C. The glass transition temperatures (T_g) for the amorphous regions, as determined by DMA, are all near 16 °C, indicating that these regions of the polymer are of similar composition. We could not probe the T_g of the semi-crystalline PE region with our instrumentation. One can also see that the crystallinity (X_C) of the materials (Fig. 1), shown in Fig. 1 increases with increasing *Mn*,. Table 1, entry 1 has *Mn* = 95 kg mol^{-1} and X_C = 0.09. Increasing *Mn* to 202 kg mol^{-1} as in entry 5 leads to an increase in X_C to 0.19. In the case of the TCPs run for 1.5–2 hours,[8] X_C, was seen to approach 0.40 which is the X_C for PE made with this catalyst system. This is consistent with a larger contribution from the C_2H_4 rich segments.

Efforts to observe microphase separation by TEM were not successful for the samples obtained in entries 1–3 of Table 1. Weakly ordered cylindrical morphologies are obtained for the higher molecular weight materials (entries 4–5, Fig. 2). The size of the cylindrical domains is smaller than those observed for the individual TCP segments, *i.e.* if one simply stops the reaction at t_1.[8] This behavior has been noted in comparisons of (AB)$_n$ multiblock copolymers of styrene and isoprene to their respective diblock copolymers, where lamellar domain sizes were seen to decrease from $n = 1$ to $n = 2$.[9] The elastomeric behavior of the polymers (Fig. 3), as probed by tensile mechanical testing shows that the samples are able to stretch to greater than 300% strain with 40–50% elastic recovery at 20 °C. Increasing *Mn* provides an increase in the maximum extension (ME), but little variation on the recovery. For example, the ME from the samples in entries 1 and 4 are 250% and 750%, respectively. Testing the elasticity at 65 °C significantly increases the elastic recovery, as shown in Fig. 2. Samples from entries 1 and 2 show the greatest improvement where recoveries of 90% or better are obtained at 100% strain and the strain at break now extends to ~1000%. Even at 1000% strain one can observe 80% recovery.

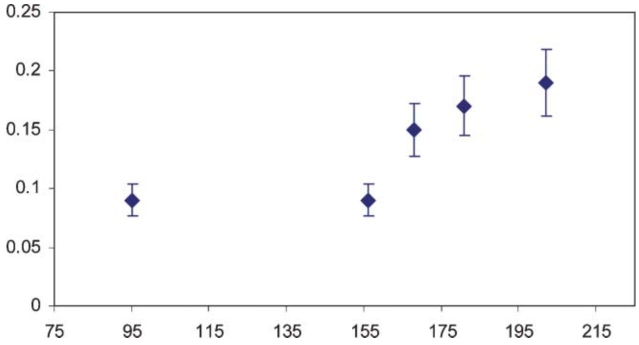

Fig. 1 Crystallinity of pseudo-tetrablock copolymers with respect to molecular weight.

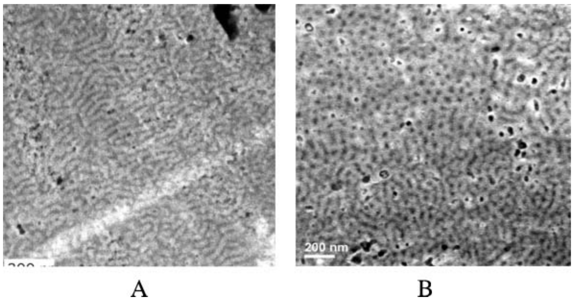

Fig. 2 TEM images of polymers obtained in (a) entry 4, (b) entry 5. The morphologies are cylindrical, where amorphous, **1**-rich cylinders (dark) are embedded in a semi-crystalline PE matrix (light). Synthesis of pseudo-tetrablock copolymers.

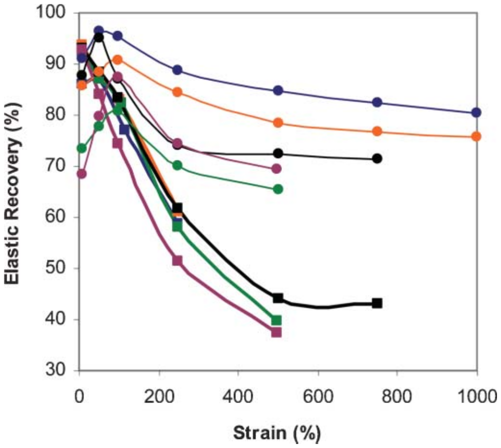

Fig. 3 Elastic recovery at 20 °C (squares) and 65 °C (circles). Entries 1–5 are represented by the blue, orange, green, black, and purple curves, respectively. The first point corresponds to 10% strain.

The increase in elastic recovery seen in increasing the testing temperature from 20 °C to 65 °C may be explained by examining the TEM micrographs for samples 4–5 in Fig. 1. The images show that the amorphous regions are essentially cylinders in a semi-crystalline PE matrix. With such a morphology, which is not typical of the good all-amorphous thermoplastic elastomers[5] like SEBS, where there are glassy spheres or cylinders in a rubbery matrix, it is not surprising that there is substantial plastic deformation of the semicrystalline PE. In these regions there is a well-formed network of lamellar crystals. That network deforms plastically and does not recover when the stress is removed.[10] Samples 1 and 2, that are partially molten at 65 °C, will recover more readily since we now have a relatively small population of crystals in the PE regions and a much less interconnected network of crystals. On stretching at this temperature it is also possible that stress induced crystallization of fibrillar crystals occurs that reinforce the predominantly elastomeric matrix in tension but which don't impede it from relaxing back to nearly its original dimensions.

It is interesting that entries 1 and 2 show no microphase separation, yet they show the best elastomeric properties. This observation has also been seen in other systems[11] involving semicrystalline hard segments leading one to conclude that microphase separation may not be required. It is also worth noting that the testing temperature of 65 °C in Fig. 2 is near the T_m of the semicrystalline region. The tapered structure likely leads to crystalline domains of various sizes. The melting peak in these polymers is broad and, although it peaks at 65 °C, there is likely a distribution of crystalline domain sizes, some which melt at above 65 °C and are responsible for anchoring the polymer network.

In summary, Scheme 1 provides a simple protocol for the synthesis of covalently bound TCP structures in which the ratio of C_2H_4 and **1** tapers as a function of chain length. Since each of the two TCP segments contains amorphous and a semicrystalline components, the final structure mimics that of tetrablock copolymers. NMR spectroscopy, GPC, DMA, and DSC are all consistent with the proposed structures. TEM examination of the samples obtained at longer reaction times confirms that the segments are sufficiently different to favour microphase separation. These copolymers show poor elastomeric properties at 20 °C. However, these properties are greatly improved at 65 °C. Interestingly, the best elastomeric properties are seen in polymers that do not microphase separate. The synthetic method in Scheme 1 should be amenable to provide various chain lengths, compositions, and thermal properties to assess the elastomeric behaviour of such polymers.†

Notes and references

† *Typical Tapered Tetrablock Copolymerization of Ethylene and 5-Norbornen-2-yl Acetate (**1**)*. A typical tetrablock polymerization was performed as follows. A metal reactor was loaded inside a glove box with **2** (20 μmol), Ni(COD)$_2$ (50 μmol), **1** (4.50 mmol), and toluene such that the final volume of this solution was 30.0 mL. An addition funnel was loaded with a solution of 4.50 mmol of **1** for the synthesis of the second tapered segment. The metal reactor and the addition funnel were sealed inside the glove box and were attached to a vacuum/nitrogen line manifold. Ethylene was fed continuously into the reactor at 200 psi and the pressurized reaction mixture was stirred at 20 °C. At a specified time (t_1) the comonomer solution in the addition funnel (pressurized by nitrogen) was added to the reaction solution. After addition of the comonomer solution was complete, the addition funnel was closed and the polymerization was allowed to run for a specified time (t_2). Ethylene was then vented and acetone was added to quench the polymerization. The precipitated polymer was collected by filtration and dried under high vacuum overnight.

Polymer Characterization. NMR spectra were obtained using Varian Unity 400 or 500 spectrometers. ^{1}H-NMR spectra of the polymers were obtained in mixed solvent (C_6D_6–1,2,4-trichlorobenzene 1 : 4 ratio in volume) at 115 °C. Incorporation of 5-norbornen-2-yl acetate was determined by summing the integration of the *exo* and *endo* ester hydrogens at δ = 4.7 and 5.0 ppm respectively and comparing to the peak for the polyethylene backbone at δ = 1.3 ppm. Gel Permeation Chromatography (GPC) measurements were performed on a Polymer Labs High Temperature GPC system (Model PL-220), with 1,2-dichlorobenzene as eluent. Differential scanning calorimetry was used to determine the thermal characteristics of the copolymers using a TA Instruments DSC 2920. The DSC measurements were recorded during the third heating–cooling cycle in the −20 °C to 180 °C range at a rate of 5 °C min^{-1}. Each sample for DSC was approximately 5 to 10 mg. The fraction of crystallinity (X_C) and the melting point (T_m) of the materials were determined in this way. Transmission electron microscopy studies were performed on annealed copolymer films. Bulk polymer samples were annealed in high vacuum for 1 day at 200 °C, followed by 3 days at 160 °C to allow the microphase to equilibrate, followed by a rapid quench in $<$1 min to liquid nitrogen temperatures. First the sample surface was cut at −190 °C to make a smooth surface for the stain to penetrate into the sample. The sample was then stained in the vapor of a 0.5% RuO_4 stabilized aqueous solution (Electron Microscopy Science) for a period of five days. Sections 80 nm thick of the stained polymer were then cut using a Leica Ultracut UCT ultramicrotome with a diamond knife at room temperature. TEM images of the stained samples were obtained using a FEI Tecnai G2 Sphera TEM operating at 200 kV. The observed contrast is due to the local oxidation of the amorphous phase of the block copolymer by RuO_4. Dynamic mechanical analysis was performed using a TA Instruments 2980 DMA. Tension film geometry was used to investigate the storage modulus, G', as a function of temperature, and to detect the glass transition of the samples by measuring tan δ. The typical sample was compression moulded into a film 0.15 mm thick. Film samples were then moved into a high-vacuum oven to be annealed for 4 days (the first at 200 °C and the remaining 3 days at 160 °C). After annealing, samples were cut into rectangle specimens $\approx$7 mm long, 1.5 mm wide and 0.15 mm thick. Both cooling and heating processes were performed at 3 °C min^{-1} for each sample. The applied frequency was 1 Hz and the applied deformation ranges were from 10–50 μm (*ie.* applied strain ranges from $\sim$0.15 to $\sim$0.7, well within the linear region of the materials) depending on the softness of the materials. Tensile mechanical testing was performed using Inston 1123 testing machine.[11] Elastic recovery is defined as the strain recovered upon unloading divided by the maximum strain reached during the step.

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