Efficient One-Pot Synthesis of diblock copolymers for the Compatibilization of HDPE/*i*PP Blends

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Abstract: An envisioned circular economy of commonly used polymers, high-density polyethylene (HDPE) and isotactic polypropylene (*i*PP), is challenging due to their immiscibility with almost all other plastics. Therefore, highly effective compatibilizers and synthetic protocols permitting their large-scale production are highly desirable. Herein, we report the efficient one-pot synthesis of strictly linear HDPE-*b*-*i*PP diblock copolymers achieved by coordinative chain transfer polymerization (CCTP). Various diblock copolymers with short and very narrow distributed HDPE (Mn = 1400–2400 g × mol^{-1}; Đ = 1.4) and long *i*PP segments were synthesized and used to compatibilize HDPE/*i*PP blends. The synthesized block copolymers differ in their overall molecular weights (Mn = 10,600–60,600 g × mol^{-1}) by varying the *i*PP segment, whereas the HDPE block was kept in a narrow range. Block copolymers with a molecular weight from Mn = 23,000–39,000 g × mol^{-1} are competitive or rather outperform the best commercial compatibilizers, INFUSE and INTUNE, with the highest efficiency in compatibilizing 30/70 (wt./wt.) HDPE/*i*PP blends by a 5 wt.-% copolymer addition. SEM studies revealed that after adding the diblock copolymer, HDPE core shell structures were formed, and the HDPE particle size decreases compared to the neat blend, avoiding HDPE particles from debonding during tensile deformation tests.

Concept

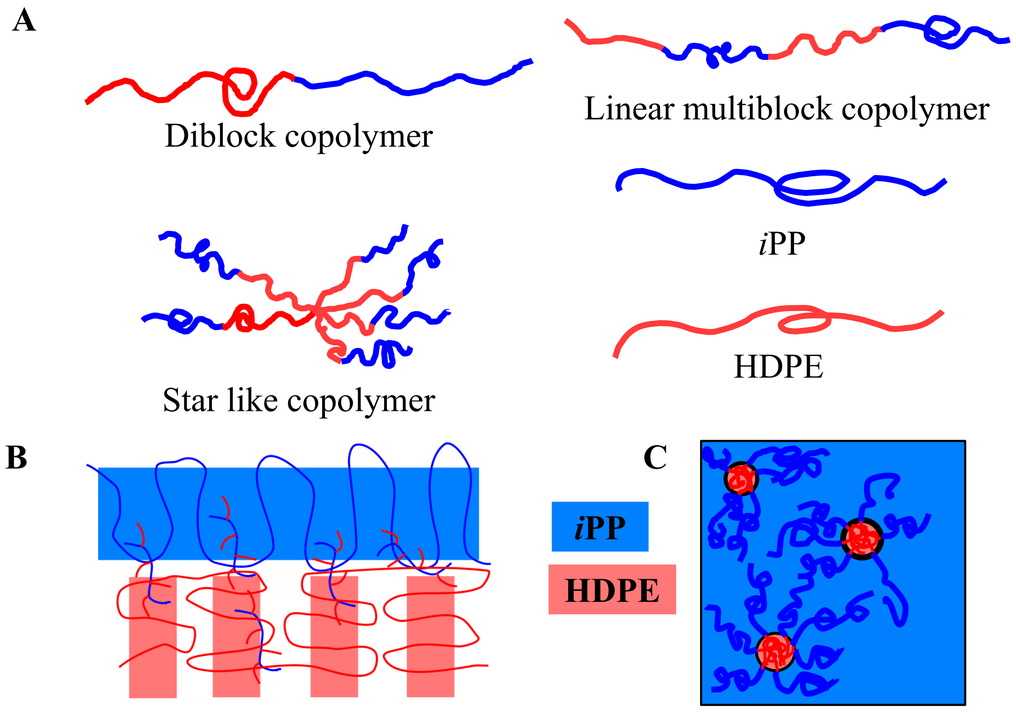
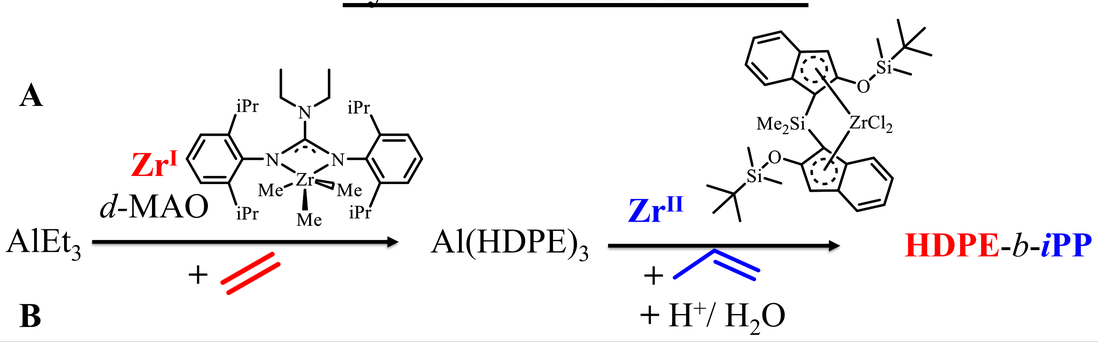


Figure 1: A) Selected nonreactive HDPE-iPP compatibilizers**; Previous work: B)** Illustration of an immiscible HDPE/*i*PP polymer−polymer interface stabilized with an in both domains cocrystallizing HDPE grafted *i*PP block copolymer. **This work: C)** HDPE-core-*i*PP-shell formation in an *i*PP matrix, stabilized by an HDPE-*b*-*i*PP diblock copolymer.

Synthesis of HDPE-*b*-*i*PP

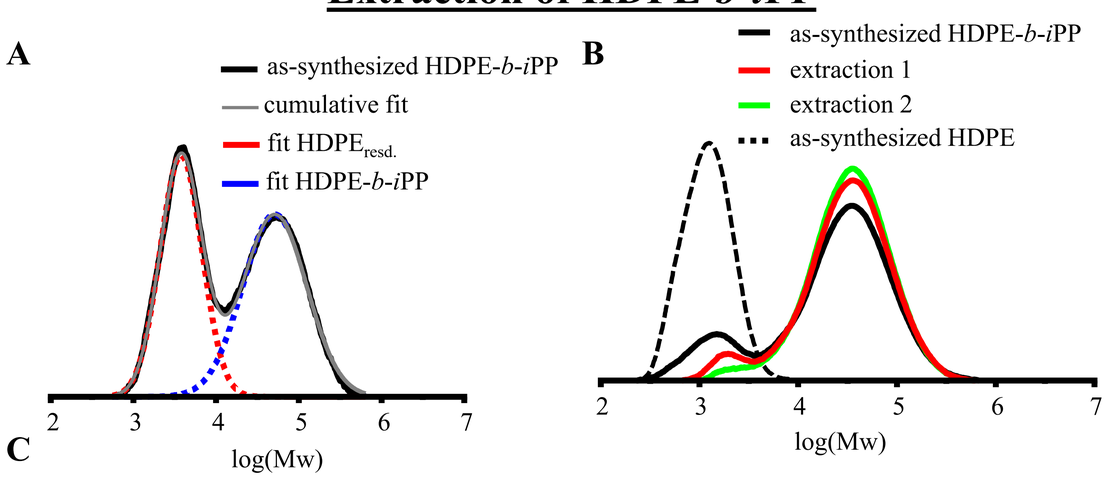


B

Entry	$V_{eth.}$ [l_n]	$V_{prop.}$ [l_n]	T_{react} [°C]	$M_{n\ HDPE}$ [g×mol]	$Đ_{HDPE}$	$M_{n\ HDPE\text{-}b\text{-}iPP}$ [g×mol]	$Đ_{HDPE\text{-}b\text{-}iPP}$	$ω_{HDPE\text{-}b\text{-}iPP}$ [wt.-%]
1	2		70	1700	1.5			
		8	50			39,500	2.2	84
2	10		70	1500	1.4			
		11	65			25,000	2.2	57
3	13		70	1500	1.3			
		12	85			11,300	2.1	57

Figure 2: A) One-pot synthesis protocol to produce HDPE-*b*-*i*PP. Step 1: Zr^{I} polymerizes ethylene and reversibly transfers the growing polymer chain to $AlEt_3$. This allows the simultaneous growth at all alkylgroups of aluminium leading to $Al(HDPE)_3$. The HDPE chain length depends solely on $AlEt_3$ concentration and ethylene conversion. The molecualar weight is controlled between 1200 g/mol (entanglement threshold) and 2800 g/mol (precipitation threshold). **Step 2:** Switching to propylene and adding Zr^{II} enables isotactic reversible chain transfer polymerization in the presence of $Al(HDPE)_3$. The *i*PP block length can be tuned via temperature and $Al(HDPE)_3$ concentration. **B) Reaction conditions:** $V_{toluene}$ = 250 ml; n_{ZrI} = 1 µmol; n_{ZrII} = 1 µmol; n_{dMAO} = 2 mmol; n_{AlEt3} = 2.80 mmol; $p_{eth.}$ = 3 bara; $p_{prop.}$ = 5 bara; Mark-Houwink parameters: K = 40.6; α = 0,725 for linear HDPE and K = 19.0; α = 0.725 for *i*PP. The molecular weight M_n and ω was determined by size exclusion chromatography and subsequent peak deconvolution.

Extraction of HDPE-*b*-*i*PP

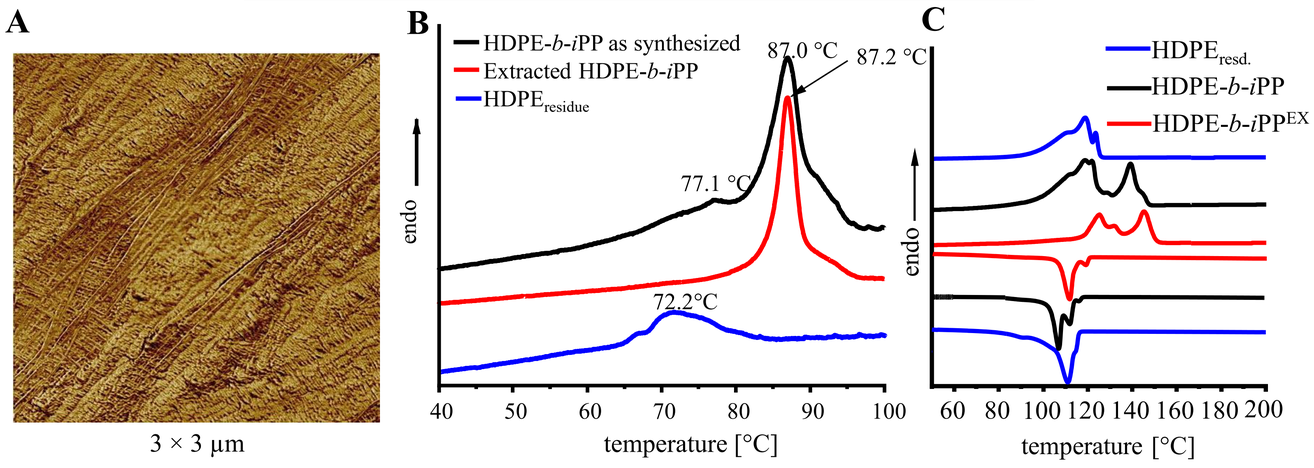


C

As-synthesized Ent.	$M_{n\ HDPE\text{-}b\text{-}iPP}$ [g×mol]	$Đ_{HDPE\text{-}b\text{-}iPP}$	$ω_{HDPE\text{-}b\text{-}iPP}$ [wt.-%]	After Extraction Ent.	$M_{n\ HDPE\text{-}b\text{-}iPP}$ [g×mol]	$Đ_{HDPE\text{-}b\text{-}iPP}$	$ω_{HDPE\text{-}b\text{-}iPP}$ [wt.-%]
1	39,500	2.2	84	1^{Ex}	39,500	2.1	98
2	25,000	2.2	57	2^{Ex}	31,300	1.8	81
3	11,300	2.1	57	3^{Ex}	23,000	1.7	71

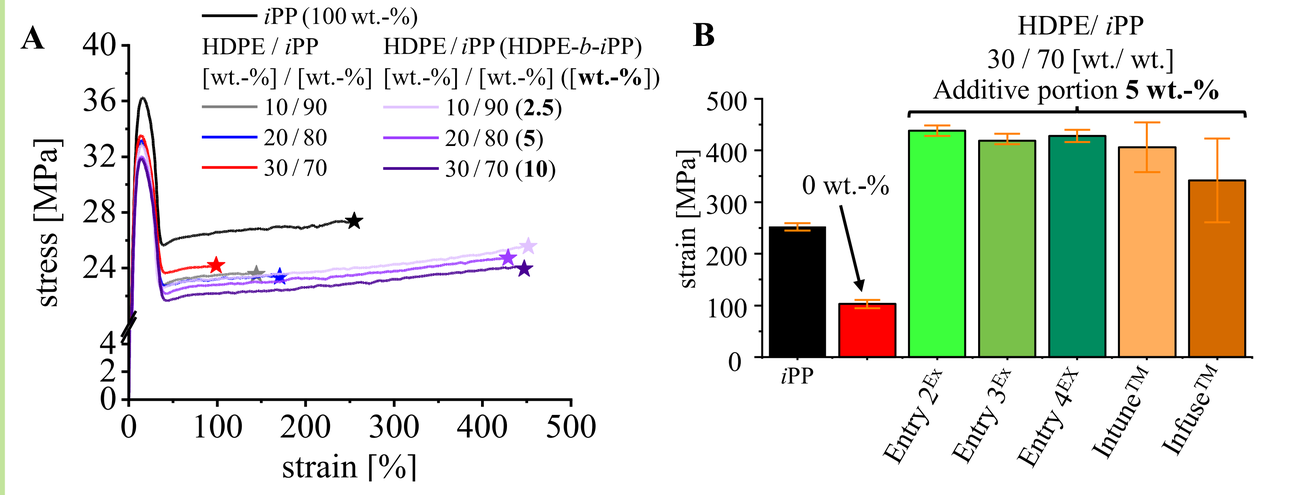
A) Peak deconvolution of molecular weight distribution for determing the amount of residual HDPE and HDPE-*b*-*i*PP. For calculation, two overlapping Gaussian curves were fitted assuming both polymers exhibit symmetrical molecular weight distributions. **B)** Size exclusion chromatography of HDPE-*b*-*i*PP monitoring the exctraction process. **C)** Results of extraction.

Characterization of extracted HDPE-*b*-*i*PP



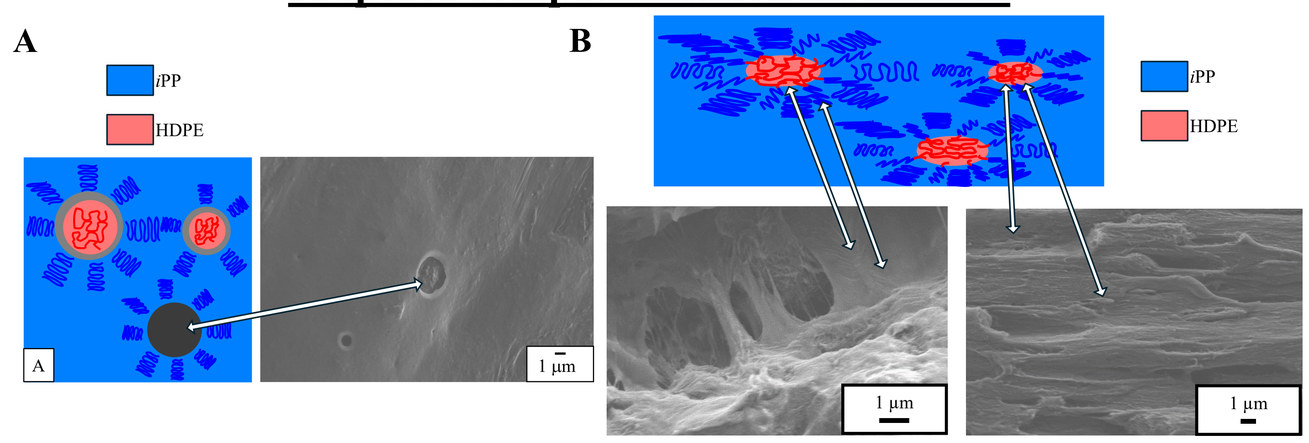
A) AFM imaging of extracted HDPE-*b*-*i*PP recveal a clear phase separation of banded spherulites of HDPE in an *i*PP matrix
B) micro-DSC in tolulene (0.5 K×min^{-1}) after extraction the second melting peak of HDPE-*b*-*i*PP (77.1 °C) vanishes and can be found in the washing solution. **C)** Differential scanning calorimetry (DSC) (10 K×min^{-1}) was used to determine the melting and crystallization behavior of HDPE-*b*-*i*PP block copolymers. In a typical HDPE-*b*-iPP raw material, up to three distinct melting and crystallization transitions were observed. After extraction, less melting peaks were observed which can be allocated to the *i*PP and HDPE blocks indicating microphase separation.

Compatibilization of HDPE/ *i*PP Blends



A) Compatibilization of HDPE/*i*PP (90/10, 80/20, 70/30 wt./wt.) blends using HDPE-*b*-*i*PP (entry 2). Lower compatibilizer loadings (2.5–5 wt.-%) are sufficient for blends with lower HDPE content (90/10 wt./wt., 80/20 wt./wt.), 10 wt.-% is required for the 70/30 blend to restore strain at break. **B)** Compatibilization of 30/70 (wt./wt.) HDPE/iPP blends with extracted HDPE-b-*i*PP diblock copolymers shows superior efficiency compared to crude HDPE-*b*-*i*PP. At only 5 wt.-%, HDPE-*b*-*i*PP even surpass the commercially avaiable compatibilizers Intune^{TM} an Infuse^{TM}.

Proposed compatibilisation mechanism



Proposed mechanism: A) Large, weakly bonded HDPE domains cause cracks and a ~200% drop in tensile strength. **B)** Addition of HDPE-*b*-iPP reduces domain size by two-thirds and restores strain at break. A core–shell morphology is proposed, with the compatibilizer anchoring HDPE particles via interfacial adsorption.

Acknowledgement

References:

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