



Synthesis and Small-Angle X-ray Scattering Investigations of Ureido-Pyrimidone Hydrogen Bonding Star and Linear Poly(ethylene-co-propylene)s

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Synthesis and Small-Angle X-ray Scattering Investigations of Ureido-Pyrimidone Hydrogen Bonding Star and Linear Poly(ethylene-co-propylene)s

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14. ABSTRACT Copolymers of poly(ethylene) and poly(propylene) having ureido-pyrimidone (UPy) hydrogen bonding moieties were synthesized and their bulk morphological behavior characterized. Anionic polymerization techniques allowed the synthesis of copolymers having well-defined linear, telechelic, and star architectures in which the UPy functional groups were located at the ends of the polymer chains. Small-angle x-ray scattering was used to characterize the bulk morphologies of these materials, which were found to be microphase separated, with the hydrogen bonding UPy moieties segregating from the copolymer bulk. The characteristic length scale observed varied substantially, depending on the molecular architecture, and is most likely correlated with the separation between microphase separated UPy-rich domains.					
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1. Introduction

Hydrogen bonding enables the introduction of thermoreversible properties into polymeric systems through the creation of specific noncovalent intermolecular interactions (1–3). The strength of these interactions is a strong function of environmental parameters such as temperature, solvent, humidity and pH. Thus, allowing control of properties through a number of the strength of hydrogen bonding associations is further tunable via structural parameters and molecular design of the hydrogen bonding sites. For instance, DNA nucleotide bases possess association constants near 100 M^{-1} , whereas synthetic multiple hydrogen bonding arrays may possess association constants as high as 10^9 M^{-1} (4, 5).

Ureido-pyrimidone (UPy) groups exhibit unusually high association constants ($6 \times 10^7\text{ M}^{-1}$ in chloroform) due to the presence of four hydrogen bonds in a configuration which minimizes repulsive interactions between opposing hydrogen bonding groups (6). This DDAA configuration (D = donor, A = acceptor) also engenders self-complementary behavior in contrast to nucleotide bases, which are complementary (A-T, G-C). The planar structure of the UPy molecule and intramolecular hydrogen bonding assists in creating and maintaining a geometry that maximizes hydrogen bonding (figure 1).

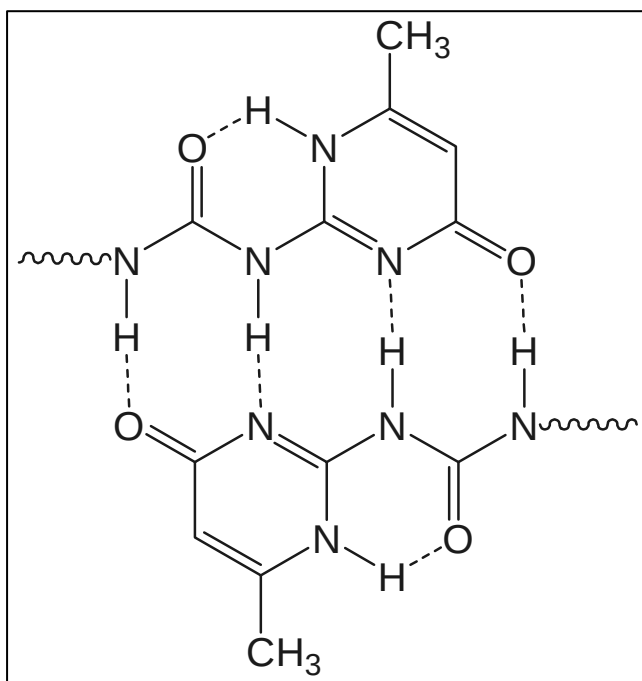


Figure 1. The UPy quadruple hydrogen bonded dimer.

The UPy hydrogen bonding group has generated interest recently as chemists have transitioned from synthesizing small molecules containing UPy to synthesizing polymers that are decorated

with the UPy moiety. Lange and coworkers demonstrated that end-functionalization of poly(ethylene glycol)/poly(propylene glycol) oligomers with UPy groups resulted in solidification of the viscous liquid precursors (7). Sijbesma et al. demonstrated chain-extension type phenomena resembling step growth polymerization in small molecules containing two UPy functional groups (8). The UPy group has a marked effect on both solution and melt viscosity. Guan et al. incorporated the UPy group into polyurethanes (9), and Yamauchi et al. introduced telechelic UPy functionality into polyesters (2). Reith et al. introduced the UPy group into polyolefins, with dramatic improvements in tensile performance (10), and Yamauchi et al. developed both random copolymers containing the UPy moiety as well as terminally functionalized polystyrenes and polyisoprenes (11, 12). The present work focuses on terminal functionality and the effect of polymer architecture on the morphology of these hydrogen bonding polymers (1).

Although significant attention has been devoted to the role of the UPy hydrogen bonding group on solution rheological performance, fewer studies have been devoted to understanding the solid state morphological implications of introducing hydrogen bonding groups. This work seeks to examine the morphology of hydrogen bonding UPy functionalized poly(ethylene-co-propylene) polymers with both linear and star architectures. The effects of functionality between linear and telechelically functionalized linear polymers and architecture between linear and star architectures are discussed. Small-angle x-ray scattering (SAXS) is a powerful technique for characterizing microphase separation induced by hydrogen bonding, as observed in polyurethanes (13). The presence of associating groups that contain heteroatoms provides an adequate electron density difference with the hydrocarbon ethylene/propylene backbone, making UPy-based hydrogen bonded structures favorable for x-ray scattering characterization.

2. Experimental

2.1 Materials

Isoprene (Aldrich, 99%) was passed through an alumina column and a molecular sieves column. Nickel octoate (Shepherd Chemicals, 8% [w/w] in mineral spirits), triethylaluminum (Aldrich, 1.4 M in hexane), palladium on activated carbon (Aldrich, 10 % [w/w]), 3-(*t*-butyldimethylsilyloxy)-1-propyllithium (TBDMSP_{Li}, FMC Corporation Lithium Division, 0.4 M in cyclohexane), ethylene oxide (Aldrich), dimethyl sulfoxide (DMSO) (Aldrich, anhydrous grade), and isophoronediiisocyanate (IPDI) (Aldrich, 98%) were used as received. Divinylbenzene (DVB) (Aldrich, 80% divinylbenzene comprising a mixture of isomers, 20% ethylvinylbenzene) was stirred over calcium hydride for 24 hr, degassed several times, and vacuum distilled (0.10 mm Hg, 23–25 °C). Divinylbenzene was then vacuum distilled from dibutylmagnesium (0.10 mm Hg, 23–25 °C). Cyclohexane (EM Science) was passed through an alumina column and a molecular sieves column immediately prior to use. Tetrahydrofuran

(THF) (EM Science, HPLC grade) was distilled from sodium/benzophenone immediately prior to use. Dibutyl tin dilaurate (DBDTL) (Aldrich, 99%) was dissolved in THF as a 1 weight-percent solution. To remove moisture, impurity 6-methylisocytosine (MIC) (Aldrich, 98%) was dried at 100 °C under vacuum overnight.

2.2 Synthesis of Linear Telechelic Polyisoprene

All polymerizations were conducted using a glass anionic reactor system, which consisted of a 600-mL heavy-walled, glass bowl, a stainless steel top plate, and stainless steel magnetically coupled mechanical stirrer. In addition to this basic assembly, the unit was equipped with a heat-exchange coil, a thermocouple, a thermistor to measure and control the temperature, a septum-sealed port and various stainless steel transfer lines to introduce isoprene (monomer) and cyclohexane (solvent), and inlet/vent for purified nitrogen. The temperature was controlled using steam/cold water passed through stainless steel coils within the 600 mL glass polymerization vessel. The system was maintained at a constant nitrogen pressure (10–15 psi).

The 600-mL reaction vessel was charged with cyclohexane (500 mL, 4.64 mol) and isoprene (45 mL, 0.44 mol) and maintained at 50 °C. TBDMSPrLi (4.47 mL, 2 mmol) was added to the solution to initiate polymerization, targeting a 15,000 g/mol polymer. The reaction was allowed to proceed for 2 hr to ensure quantitative conversion. Degassed methanol was added to terminate the polymerization and generate monofunctional polyisoprenes. An excess of ethylene oxide was bubbled through the polymerization solution and allowed to react for 30 min to prepare telechelic polyisoprenes. The polymerization was terminated using degassed methanol. ¹H NMR (400 MHz, CDCl₃, δ): 5.1 ppm (b, 1,4-polyisoprene), 4.75 ppm (b, 3,4-polyisoprene), 3.6 ppm (t, CH₂-O-Si(CH₃)₂(C(CH₃)₃), 1.0 – 2.2 (b, -CH₃, -CH₂-, CH in polyisoprene units), 0.9 ppm (s, CH₂-O-Si(CH₃)₂(C(CH₃)₃), 0.04 ppm (s, CH₂-O-Si(CH₃)₂(C(CH₃)₃). Monomer conversion was greater than 90%, and ¹H NMR indicated that the microstructure of the polymer was ~92% 1,4-enchainment and 8% 3,4-enchainment.

2.3 Synthesis of Star-Shaped Telechelic Polyisoprene

The 600-mL reaction vessel was charged with cyclohexane (500 mL, 4.64 mol) and isoprene (45 mL, 0.44 mol) and maintained at 50 °C. TBDMSPrLi (4.47 mL, 2 mmol) was added to the solution to initiate polymerization, targeting a 15,000 g/mol polymer. The reaction was allowed to proceed for 2 hr. After 2 hr, an aliquot was removed and terminated with degassed methanol. DVB (1.89 mL, 10.7 mmol) was added to the solution to couple the polyisoprene arms. The reaction was allowed to proceed overnight. The reaction was terminated via the addition of degassed methanol. ¹H NMR assignments corresponded to those from linear polyisoprene, and resonances for divinylbenzene were not observed, presumably due to immobility in the star core. Monomer conversion was greater than 90%, and size exclusion chromatography (SEC) indicated greater than 95% coupling of the arms to star polymer.

2.4 Hydrogenation of Polyisoprene Linear Polymers

A linear polyisoprene (18 g) was dissolved in cyclohexane (110 mL) and added to a 500-mL pressure vessel. Pd/C (2.5 g) catalyst was added, and the reactor was pressurized with hydrogen and vented three times. The vessel was pressurized with hydrogen (50 psi) and heated to 100 °C for 24 hr. The Pd/C catalyst was removed using filtration through Celite. The cyclohexane solution was concentrated to 100 mL in vacuo. The polymer solution was then precipitated into isopropanol (600 mL) and dried in vacuo at 60 °C for 24 hr. ^1H NMR (400 MHz, CDCl_3 , δ): 3.6 ppm (t, $\text{CH}_2\text{-O-Si}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$), 1.0 – 2.0 (b, $-\text{CH}_3$, $-\text{CH}_2-$, CH in poly(ethylene-co-propylene) units), 0.9 ppm (s, $\text{CH}_2\text{-O-Si}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$), 0.04 ppm (s, $\text{CH}_2\text{-O-Si}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$). Percent yield, which was determined gravimetrically, was between 60% and 85%, and ^1H NMR indicated complete hydrogenation.

2.5 Synthesis of Preformed Nickel Hydrogenation Catalyst

Cyclohexane (15 mL) and nickel octoate (0.228 g, 0.66 mmol) were added to a septum-sealed 100-mL, round-bottomed flask purged with nitrogen. Triethylaluminum (1.36 mL, 9.9 mmol) was added dropwise to the nickel solution. An opaque, black colloidal suspension formed immediately and was allowed to age for 15 min at room temperature under a nitrogen atmosphere to form a homogeneous solution.

2.6 Hydrogenation of Polyisoprene Star-Shaped Polymers

A polyisoprene star polymer (3.0 g, 0.02 mmol) and a preformed nickel catalyst (approximately 20 mL, 0.10 mmol) were dissolved in cyclohexane (500 mL) and added to a 600-mL reactor. The reactor was pressurized with hydrogen and vented three times. The vessel was pressurized with hydrogen (90 psi) and heated to 50 °C for 24 hr. The nickel catalyst was extracted from the polymer solution with three citric acid (Aldrich, 98%, 500 mL, 50 mmol) washes following quantitative hydrogenation. The cyclohexane solution was concentrated to 100 mL, precipitated into isopropanol (600 mL), and dried in vacuo at 60 °C for 24 hr. ^1H NMR assignments corresponded to those of hydrogenated linear polyisoprene. Quantitative hydrogenation of the arms was confirmed by ^1H NMR spectroscopy, and recovered yield was 84%.

2.7 Removal of Protecting Group From Poly(ethylene-co-propylene)

The poly(ethylene-co-propylene) (1.0 g, 0.007 mmol) was dissolved in THF (50 mL), and concentrated hydrochloric acid (10 M, 5 mL) was added to the solution. The solution was allowed to stir for 18 hr at 50 °C and precipitated into isopropanol twice to remove residual hydrochloric acid. The polymer was then dried at 60 °C under vacuum for 24 hr. ^1H NMR (400 MHz, CDCl_3 , δ): 3.6 ppm (t, $\text{CH}_2\text{-OH}$), 1.0 – 2.0 (b, $-\text{CH}_3$, $-\text{CH}_2-$, CH in poly(ethylene-co-propylene) units). ^1H NMR confirmed complete deprotection of the hydroxyl groups, with an isolated yield of approximately 85%.

2.8 Functionalization of Polymers With UPy Groups

After quantitative deprotection of poly(ethylene-co-propylene) was achieved, the UPy terminal group was attached in two steps. In the first step, the poly(ethylene-co-propylene) (1.0 g, 0.007 mmol) was dissolved in freshly distilled THF (3.5 mL) and DBDTL catalyst (0.01 mL, 0.017 mmol) was added. IPDI (0.29 mL, 1.36 mmol) was added to the solution, and reaction was allowed to proceed for 72 hr at 60 °C to ensure complete conversion. In the second step, MIC (0.38 g, 3 mmol) was added under nitrogen flush, and anhydrous DMSO (0.5 mL) was added as a cosolvent. The reaction proceeded under nitrogen at 60 °C for 72 hr. The reaction solution was quenched using excess methanol and filtered in order to isolate the polymer. The product was dissolved in chloroform and filtered again in order to remove residual MIC. The polymer was precipitated into methanol, collected, and dried in vacuo. Residual MIC, IPDI, and coupled products were quantitatively removed through repeated filtration and selective solvent precipitation. ^1H NMR (400 MHz, CDCl_3 , δ): 12.9 – 13.2 (s, $-\text{NH}-\text{C}(\text{CH}_3)=$ in UPy units), 11.8 – 12.1 (s, $-\text{NH}-\text{C}=\text{N}$ -in UPy units), 10.4 – 10.7 (s, $-\text{CH}_2\text{NH}-\text{CO}-$ in UPy units), 5.7 – 6.0 (s, $\text{NHC}(\text{CH}_3)=\text{CHO}-$ in UPy units), 1.0 – 2.0 (b, $-\text{CH}_3$, $-\text{CH}_2-$, CH in poly(ethylene-co-propylene) units). Following the two-step functionalization, the recovered yield was between 80% and 85%, and ^1H NMR indicated 75%–100% functionalization of the hydroxyl groups with the UPy units.

2.9 Polymer Characterization

^1H NMR spectra were collected in CDCl_3 at 400 MHz with a varian unity spectrometer. Glass transition and melting temperatures were determined using a Perkin-Elmer Pyris 1 cryogenic differential scanning calorimeter (DSC) at a heating rate of 20 °C/min under nitrogen, which was calibrated using indium ($T_m = 156.60$ °C) and zinc ($T_m = 419.47$ °C). Glass transition temperatures were reported as the transition midpoint during the second heat. Molecular weights were determined at 40 °C in THF (HPLC-grade) at 1 mL/min using polystyrene standards on a Waters 717 + Auto-sampler SEC equipped with 3-in-line, 5- μm PLgel MIXED-C columns, a Waters 2410 refractive index detector operating at 880 nm, and Wyatt Technologies miniDAWN multiple angle laser light scattering (MALLS) detector operating at 690 nm, which was calibrated with polystyrene standards. The refractive index increment (dn/dc) was calculated online. All molecular weight values reported were absolute molecular weights obtained using the MALLS detector. SEC analysis was not reliable for star-shaped UPy functional polymers due to their association at SEC concentrations in THF, which was verified using dynamic light scattering.

2.10 SAXS Measurements

UPy functional poly(ethylene-co-propylene) polymers were dissolved in THF and cast in Teflon* molds. The films were dried in a vacuum oven and stored at -15 °C until use. $\text{Cu}_{K\alpha}$ x-ray

*Teflon is a registered trademark of Dupont Engineering Polymers.

radiation was generated using a Rigaku Ultrax18 rotating anode x-ray generator operated at 40 kV and 115 mA. A nickel filter was used to eliminate all wavelengths but the $\text{Cu}_{K\alpha}$ doublet, with an average wavelength of $\lambda = 1.542 \text{ \AA}$. The 3-m camera used three pinhole collimation (300, 200, and 600 μm), with a sample-to-detector distance of approximately 1.5 m. Two-dimensional (2-D) data sets were collected using a molecular metrology 2-D multiwire area detector. The data were corrected for detector noise, sample absorption, and background scattering, followed by azimuthal averaging to obtain intensity as a function of the scattering vector, $I(q)$, where $q = 4\pi \cdot \sin(\theta)/\lambda$ and 2θ is the scattering angle. The data were then placed on an absolute scale using a type 2 glassy carbon sample 1.07 mm thick, previously calibrated at the Advanced Photon Source in the Argonne National Laboratory, IL, as a secondary standard. All data processing and analysis were done using Wavemetrics IGOR Pro 5.04 software and IGOR procedures written by Dr. Jan Ilavsky of Argonne National Laboratory.

3. Results and Discussion

3.1 Polymer Structure and Expected Association

Anionic polymerization with a protected hydroxyl functional initiator enabled the synthesis of well-defined linear, telechelic, and star-shaped polymers. The subsequent deprotection of the hydroxyl group and reaction with hydrogen bonding precursors led to novel UPy-containing linear monofunctional, telechelic, and star polymers (1). The molecular weight characterization of the hydrogen bonding polymers under study is shown in table 1. The association of UPy functionalized polymers during SEC limited the use of SEC in characterizing the final polymers; thus, SEC data from the precursor polymers is given.

Table 1. Molecular weight and molecular weight distribution of monofunctional, telechelic, and star polyisoprene after each functionalization step.

Polymer Topology	Polymer	M_n^a	M_w/M_n^a
Linear monofunctional	12K mono	14,800	1.04
	24K mono	23,000	1.04
Linear telechelic	12K tele	11,000	1.05
	24K tele	24,300	1.08
Star	90K star	90,700	1.37

^a Determined using SEC at 40 °C in THF with a MALLS detector; precursor molecular weights.

Due to the strong tendency of UPy groups to dimerize, different architectures and functionalities of the polymers would be expected to produce differently associated structures (figure 2). The monofunctional linear polymer would be expected to produce a simple dimer in solution, with twice the molecular weight of the original polymer. The telechelically functionalized linear polymer should form extended chains with a degree of polymerization, depending on the strength of the association. The star polymer with peripheral functionality is expected to form a noncovalent network structure.

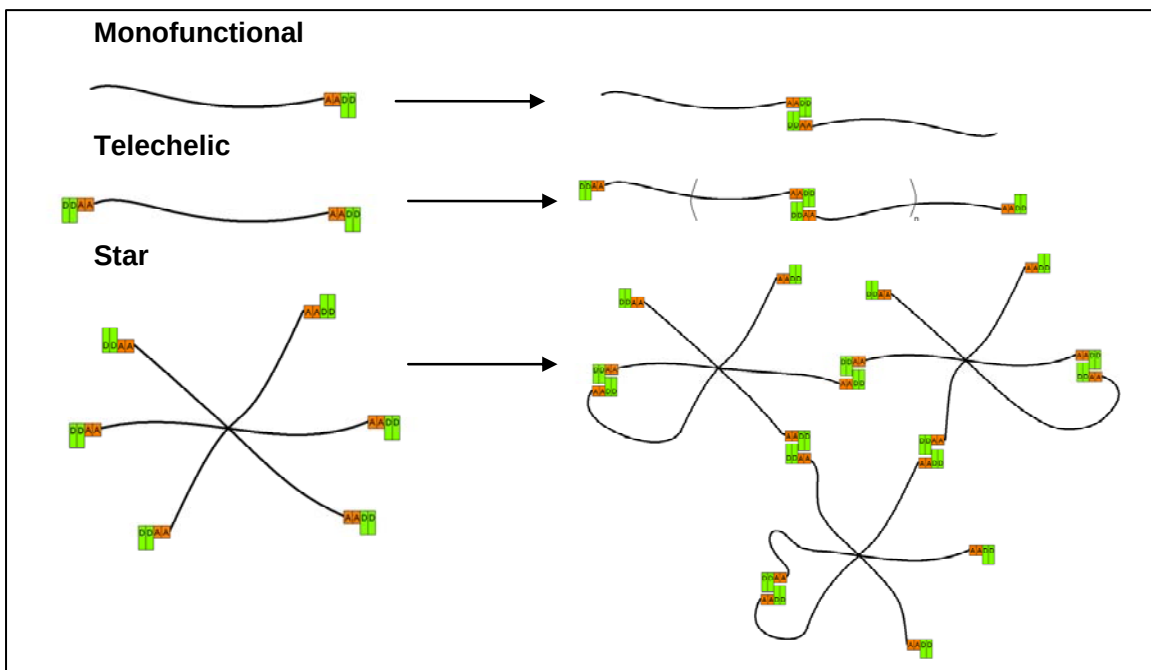


Figure 2. Representation of expected modes of association for different hydrogen bonding architectures.

3.2 SAXS Results

The hydrogen bonding ethylene-propylene copolymers bearing terminal functionality generated interesting scattering profiles, as shown in figure 3. In general, all samples exhibited a single scattering maximum, establishing the presence of a nanometer-scale structure within the samples, most likely microphase separation of the hydrogen bonding domains within the ethylene-propylene polymer bulk. The presence of microphase separation in the absence of solvent in these polymers suggests associations of greater than two UPy groups, a conclusion which is supported in previous rheological and DSC studies of telechelic UPy polyisoprenes by Yamauchi et al. (11).

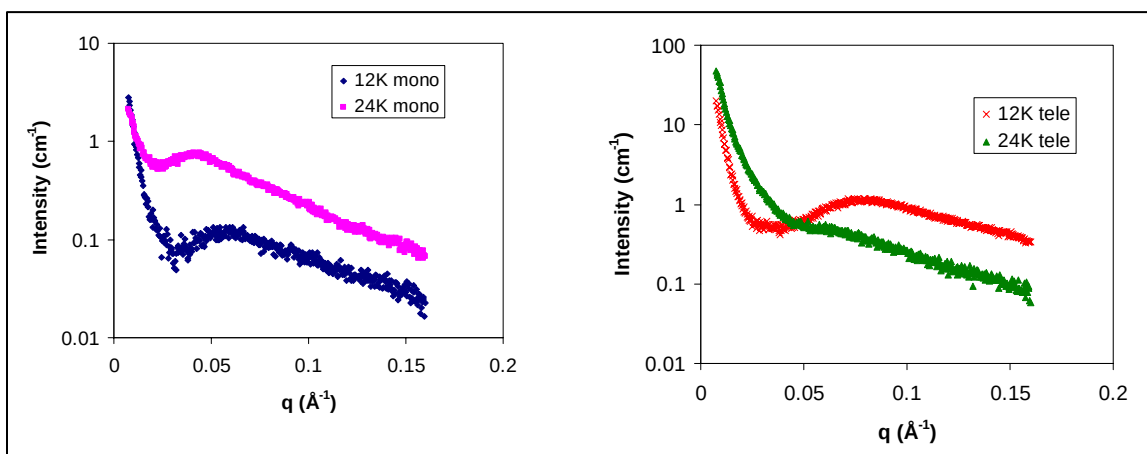


Figure 3. SAXS data for UPy-containing monofunctional (left chart) and telechelic (right chart) poly(ethylene-co-propylene)s polymers.

The hydrogen bonding polymers exhibited interesting trends in the position of the scattering maxima with respect to molecular weight and architecture. The positions of the scattering maxima, q^* , were calculated by fitting the sum of a Gaussian peak shape and a linear baseline to the scattering data. The positions of the maxima were then used to determine the Bragg spacing, $d = 2\pi/q$, given in table 2. One trend observed was a shift in the position of the scattering maxima to lower angles (or larger spacings) with increasing molecular weight (figure 3). This was anticipated as the molecular weight between UPy groups should correlate to the distance between UPy-rich domains in a microphase separated morphology. The trend is observed for the monofunctional and telechelic polymers.

Table 2. Scattering maxima and corresponding Bragg spacings.

E/P M_n	Architecture	q^* ($\text{\AA}^{-1}$)	D (nm)
12K	Mono	0.058	10.8
12K	Tele	0.078	8.1
24K	Mono	0.041	15.5
24K	Tele	0.046	13.6
91K (12K arms)	Star	0.074	8.5

Upon examining the scattering data as a function of architecture, it appears that transitioning from monofunctional linear to telechelic linear functionality resulted in a shift of the maxima to higher angles (smaller real-space correlation distances), as can be seen in figure 4. This effect was consistently observed for samples of different molecular weight and seems to be the result of increasing the overall concentration of hydrogen bonding groups while holding the molecular weight of the polymer constant. For example, the 12 kg/mol telechelically functionalized polymer has twice the number of UPy moieties per mol polymer than does the monofunctional 12 kg/mol polymer. Alternatively, the 12 kg/mol telechelically functional polymer may be viewed as two 6K monofunctional polymer chains joined at their nonfunctional ends.

The 90 kg/mol poly(ethylene-co-propylene) star polymer produced a single scattering maximum similar to those observed for the other materials (figure 5). The position of this peak exists at a higher q value than the positions of the scattering maxima for the 12 kg/mol monofunctional or the 24 kg/mol telechelic polymers, suggesting an even smaller distance between microphase separated domains of the hydrogen bonding UPy groups. The star architecture can be viewed as a collection of linear, monofunctional 12 kg/mol arms joined together at their nonfunctional termini. The presence of intramolecular association is highly probable in the case of the star polymer, which would also decrease the dimensions of the star polymer molecules.

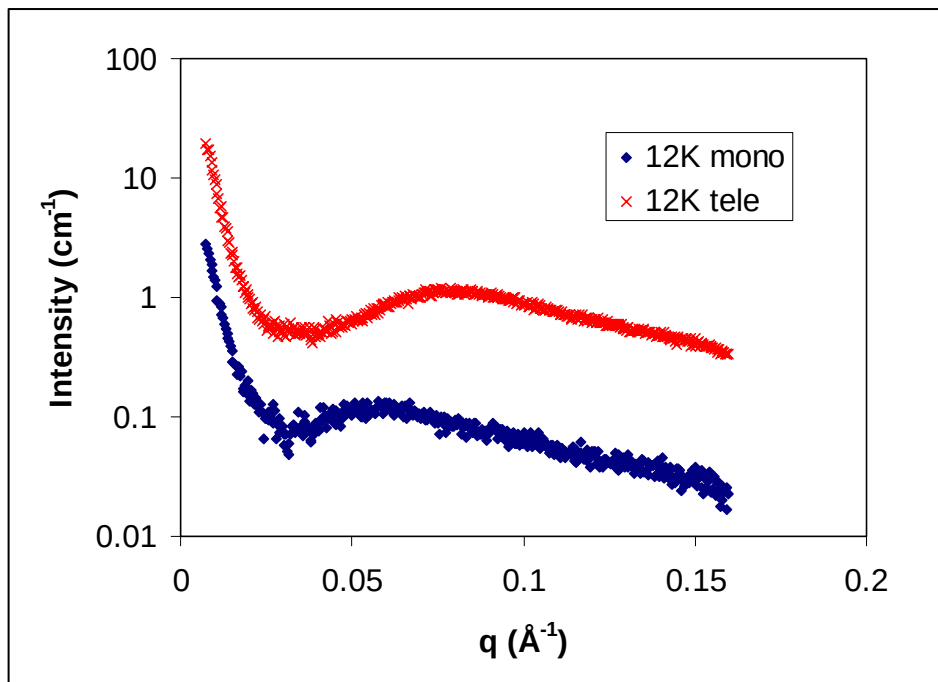


Figure 4. SAXS data showing the effect of functionality for 12 kg/mol polymers.

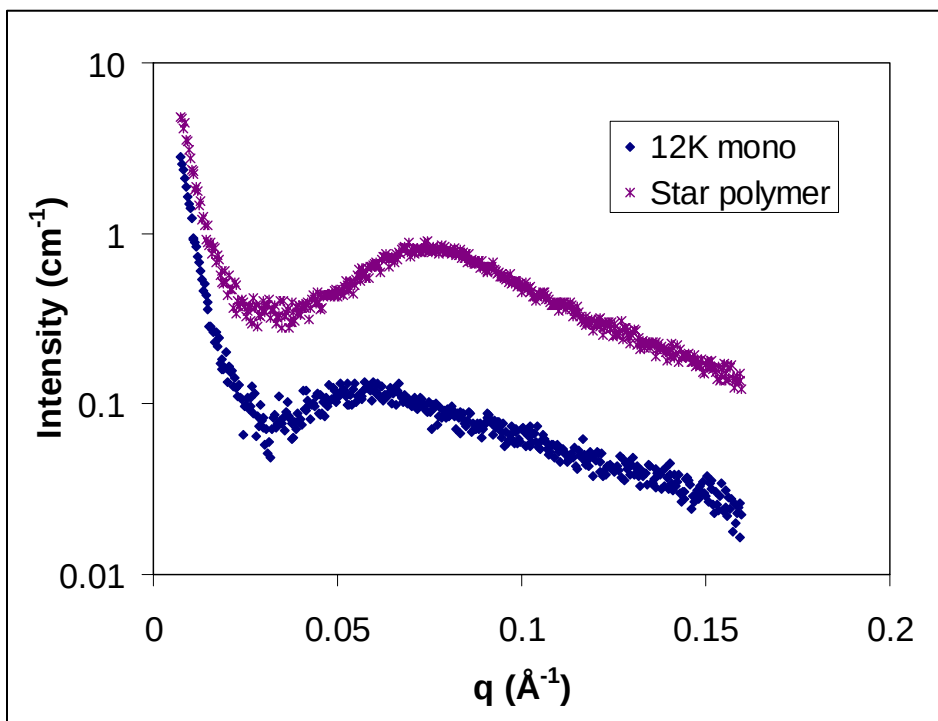


Figure 5. Scattering profile for star-shaped poly(ethylene-co-propylene) with UPy functional periphery and the 12K monofunctional polymer.

4. Conclusions

UPy-functionalized linear and star-shaped polymers were found to be microphase separated, as determined from small-angle x-ray scattering studies. The maxima in the SAXS data are thought to arise from interdomain scattering by the microphase separated UPy groups within the ethylene-propylene hydrocarbon matrix. The presence of microphase separated domains in these materials suggested a clustering of the hydrogen bonding groups beyond simple dimerization, which would be unlikely to produce a clear correlation peak in SAXS. The Bragg spacings corresponding to the scattering maxima followed trends with molecular weight and architecture, which were explainable from a molecular level. Specifically, increased molecular weight between UPy groups led to an increased spacing between domains, while increased functionality in going from monofunctional to telechelic polymers led to decreased spacings between microphase separated domains.

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AT AUSTIN
3925 W BRAKER LN
AUSTIN TX 78759-5316

1 DIRECTOR
US ARMY RESEARCH LAB
IMNE ALC IMS
2800 POWDER MILL RD
ADELPHI MD 20783-1197

3 DIRECTOR
US ARMY RESEARCH LAB
AMSRD ARL CI OK TL
2800 POWDER MILL RD
ADELPHI MD 20783-1197

3 DIRECTOR
US ARMY RESEARCH LAB
AMSRD ARL CS IS T
2800 POWDER MILL RD
ADELPHI MD 20783-1197

ABERDEEN PROVING GROUND

1 DIR USARL
AMSRD ARL CI OK TP (BLDG 4600)

NO. OF
COPIES ORGANIZATION

- 1 ARMY RESEARCH OFFICE
AMSRD ARL RO PC
D KISEROW
PO BOX 12211
RTP NC 27709-2211
- 3 VIRGINIA POLYTECHNIC INST AND
STATE UNIV
DEPT OF CHEMISTRY
T LONG
2110 HAHN HALL (0344)
BLACKSBURG VA 24061

ABERDEEN PROVING GROUND

- 4 DIR USARL
AMSRD ARL WM
J SMITH
AMSRD ARL WM M
CHIEF
AMSRD ARL WM MA
CHIEF
F BEYER

INTENTIONALLY LEFT BLANK.