Correlating the mechanical and surface properties with the composition of triblock copoly(2-oxazoline)s†

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The elastic moduli, surface energies, and phase morphologies of poly(2-oxazoline) triblock copolymers were investigated and compared to the corresponding homopolymers and diblock copolymers, at a constant degree of polymerization. The elastic moduli of ABA triblock copolymers were bound by those of the respective AB diblock copolymers and A homopolymers. These results show that the elastic moduli of these copolymers – obtained by instrumented indentation – depended on the interplay between phase-separation, crystallization and hygroscopicity, and can be adjusted by tailoring the composition. The surface energy strongly depended on the presence of a poly(2-nonyl-2-oxazoline) block. If such a block was present, the surface energy was reduced due to segregation of nonyl side-chains to the surface. This segregation was promoted by annealing. The crystallization of nonyl side-chains at the surface promoted the development of surface texture and an increase in surface roughness, as demonstrated by atomic force microscopy topographic imaging.

Introduction

Block copolymers with a defined degree of polymerization and a narrow molecular weight distribution can be synthesized *via* cationic ring-opening polymerization (CROP)[1–3] combined with sequential addition of the monomers.[4,5] Wiesbrock *et al.*[4] and Hoogenboom *et al.*[6] showed that the synthesis of poly(2-oxazoline)s and block copoly(2-oxazoline)s can be accelerated by using a monomodal microwave oven to heat the polymerization solution. Homopolymers, consisting of 100 units per macromolecule, and diblock copoly(2-oxazoline)s consisting of 50 units per block were synthesized, employing four different side-groups: methyl, ethyl, nonyl and phenyl.[4] Later, a triblock copolymer library was also synthesized based on the same monomers, aiming at 33 units per block in order to keep the total number of repeat units consistent with the homopolymers and diblock copolymers.[5]

Depth-sensing or instrumented indentation, a mechanical characterization technique that records the force and displacement of a geometrically defined indenter during loading and unloading of a material surface,[7,8] can be used to probe the elastic properties of polymeric materials.[9–11] This approach is particularly advantageous when the materials are prepared in small volumes, such as the dropcast thin films or spots in the present work. Using this technique, the elastic properties of the homopoly(oxazoline)s and diblock copoly(2-oxazoline)s were investigated.[12] It was observed that the polymers containing poly(2-nonyl-2-oxazoline) exhibited a lower elastic modulus than those lacking poly(2-nonyl-2-oxazoline), since the poly(2-nonyl-2-oxazoline) was above its glass transition temperature T_g during the room-temperature measurements. However, due to the appreciable crystallinity within this nonyloxazoline phase at room temperature, the elastic modulus of the poly(2-nonyl-2-oxazoline) homopolymer was ~1 GPa (considerably stiffer than expected for a polymer in its rubbery state). Furthermore, a relatively high stiffness at low humidity was found for the poly(2-methyl-2-oxazoline) homopolymer. This high stiffness was attributed to intermolecular polar interactions or hydrogen bonding. At higher humidity, poly(2-methyl-2-oxazoline) and poly(2-ethyl-2-oxazoline) take up moisture from the surrounding atmosphere, resulting in decreased stiffness.[12]

The surface energies of these homopolymers and diblock copolymers were also determined.[13] The surface energy of all diblock copoly(2-oxazoline)s with a poly(2-nonyl-2-oxazoline) block was ~21 mN m^{-1}, while all diblock copolymers without a nonyloxazoline block had a surface energy of ~45 mN m^{-1}. In agreement with other work,[14–16] this difference in surface energies was attributed to segregation of the nonyl side-chains to the surface.[13]

In the current work, the elastic moduli, surface energies and (surface) phase morphologies of triblock copoly(2-oxazoline)s are presented and related to their chemical composition. The finer increments in the chemical composition compared to the diblock copolymer series allow for a more detailed investigation of the correlations between properties and chemical composition.

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Experimental

Instrumented indentation

The instrumented indentation protocol and the sample preparation for the indentation measurements are discussed elsewhere.[12] In brief, three identical glass slides were prepared by dropcasting concentrated triblock copoly(2-oxazoline) solutions onto each glass slide. Typical diameter and height of the dropcast spots after drying were 2.5 mm and 300 μm, respectively. On selected members of the triblock copolymer library, indentation experiments were performed.[17] On one sample-slide, three indentation experiments (spaced 30 μm apart) were performed on each material using a NanoTest600 (Micro Materials Limited, Wrexham, UK) equipped with a spherical diamond indenter of 4.1 μm radius and employing 2 mN as the maximum load. On the two other replicate sample-slides, ten indentation experiments (spaced 50 μm apart) were performed using a TriboIndenter (Hysitron, Minneapolis, MN, USA) with a Berkovich tip and employing load levels decreasing from 3 mN to 300 μN in steps of 300 μN.[12] The reduced moduli E_r were obtained from the load–displacement response upon unloading employing the method proposed by Oliver and Pharr.[7] The contact depth and area of the indents were, even for the lowest loads, at least 150 nm and 0.95 μm^2 respectively. Furthermore, the strained material volume extended much deeper than the indent itself. As the indentation length scales were much larger than the lengths of the polymer chains studied (smaller than 40 nm in completely stretched conformation), the 'composite' stiffness of the phases present in the material is obtained.

The humidity was kept at 9.0 ± 1.0% and at 5.4 ± 0.4% in the NanoTest600 and the TriboIndenter enclosures, respectively. These humidities are comparable to those used during the previously reported, corresponding diblock copoly(2-oxazoline) measurements.[12] Some of the polymer spots of the triblock copolymer library exhibited an irregular shape, *e.g.* a non-circular circumference, cracks or a ridge within the spot. Such morphological irregularities make it more difficult to find a suitable region on the sample surface that is perpendicular to the indentation axis, consistent with the normal contact loading assumed in data analysis used to extract the elastic moduli from the load-depth responses. In order to improve the data quality, for the Berkovich series results are only reported if the difference in moduli obtained on duplicate sample-slides was <10%.

Considering that the Poisson's ratios ν of these polymers are not precisely known and in order to facilitate the comparison with earlier work,[12] reduced elastic moduli of indentation E_r are presented. E_r exceeds the elastic modulus observed by indentation $E_{i,sample}$ by a factor related to ν and the elastic constants of the indenter tip (diamond, $E_{diamond} = 1140$ GPa and $\nu_{diamond} = 0.07$):

$$\frac{1}{E_r} = \frac{\left(1 - \nu_{sample}^2\right)}{E_{i,sample}} + \frac{\left(1 - \nu_{diamond}^2\right)}{E_{diamond}} \quad (1)$$

As ν is between 0.45 and 0.35, E_r exceeds $E_{i,sample}$ by 14 to 25% for these data in which we have employed diamond indenters. For polymers, $E_{i,sample}$ also tends to exceed the elastic modulus E of the material obtained *via* uniaxial tension/compression due to factors such as pile-up around the indent perimeter and non-linear elastic behavior.[11,18]

Contact angle measurements

The surface energy (SE) of the triblock copolymers was determined by contact angle measurements. These measurements were performed on polymer films prepared by spin-coating of chloroform solutions (20 mg mL^{-1}) of the polymer on precleaned microscopy slides at 1000 rpm for 90 s using a WS-400/500 series spin-coater from Laurell Technologies Corp. For the contact angle measurements, the triblock copolymer films needs to be very flat and laterally larger than for the indentation experiments, explaining the difference in sample preparation. An automated OCA30 optical contact angle measuring instrument from Dataphysics was used to determine the contact angles of both diiodomethane and ethylene glycol as apolar and polar test liquids, respectively,[13] using Neumann's equation of state to calculate the surface energy.[19]

Annealing of the spin-coated films was performed in an oven for the duration and temperature indicated. The films were allowed to cool slowly to room temperature before measuring the surface energy again.

Atomic force microscopy

For the spin-coated triblock copolymers, atomic force microscopy (AFM) imaging was conducted in tapping mode in order to investigate the morphologies of the films and the influence of annealing on the morphology. A Nanoscope IIIa Multimode AFM (Digital Instruments, Santa Barbara, CA, USA) equipped with commercially available silicon tips (NT-MDT, Russia) with a force constant and resonance frequency of 5.5–11 N m^{-1} and 190–255 kHz, respectively, was used. The scan rate was 1 line per second.

Results

Mechanical properties

In order to avoid variation of the glass transition temperature (and thus, possibly, of the elastic modulus) due to changes in the total number of repeat numbers,[20,21] the total degree of polymerization for the triblock copolymers was maintained constant at 100 repeat units, which is similar to that of the corresponding diblock library.[4] This constant degree of polymerization, resulting in nominally 33 units per block for the triblock copolymers, allowed for a fair comparison of the homopolymers, diblock and triblock copolymers.

As the stiffness of materials containing poly(2-nonyloxazoline), referred to hereafter as Non, differs much from those of the materials without Non,[12] the combinations of 2-nonyloxazoline with the three other monomers were investigated first. In Fig. 1, the reduced elastic moduli E_r, which were calculated from the unloading branch of the load–displacement responses (see ESI†), are shown as a function of weight fraction Non. These weight fractions were calculated using the number of repeat units determined by ^{1}H NMR spectroscopy[4,5] and the masses of the repeat units (85, 99, 197 and 147 g mol^{-1} for 2-methyl, 2-ethyl, 2-nonyl, and 2-phenyl-2-oxazoline, respectively).

An increase in Non content resulted in a decrease in stiffness (Fig. 1). This change in stiffness results from the decreasing volume fraction of the glassy phase and the increasing volume

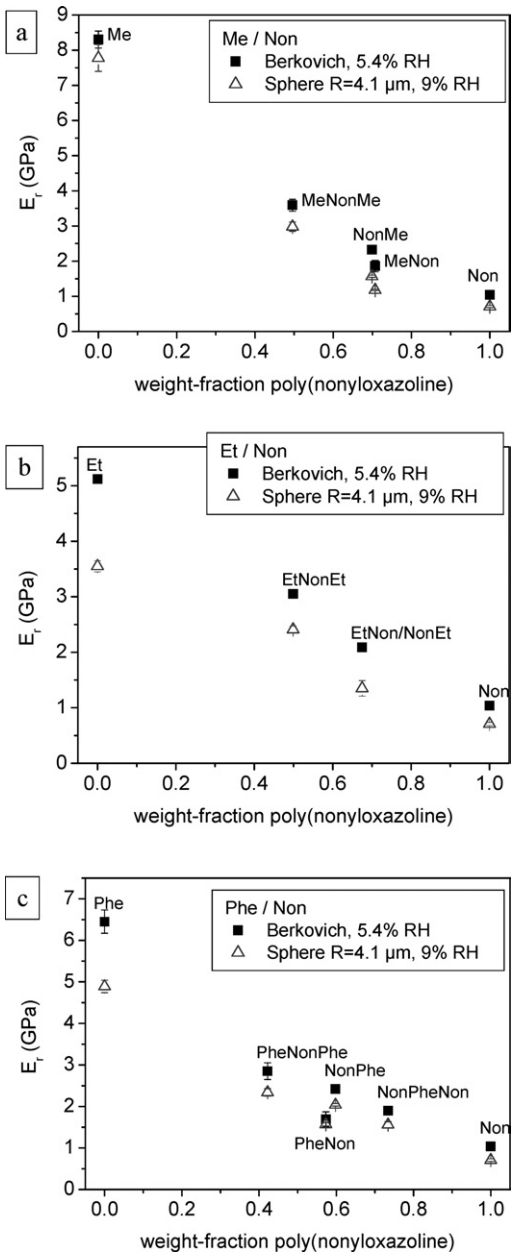

Fig. 1 Stiffness of the homopolymers, diblock and triblock copolymers with, in total, 100 repeat units, for the (a) Me–Non, (b) Et–Non and (c) Phe–Non combinations measured using a spherical or a Berkovich indenter at reduced relative humidity, RH. Standard deviations may be smaller than the symbols.

fraction of the more compliant, nonyloxazoline-rich semi-crystalline phase. The presence of these amorphous and crystalline phases was shown by differential scanning calorimetry, DSC.[4,5] Moreover, as discussed in earlier work on 2-ethyl-2-oxazoline/2-nonyl-2-oxazoline diblock copolymers with varying block lengths,[22] the stiffness of the phases is influenced by their exact chemical composition. Fig. 1a shows the homopolymers, diblock copolymers and triblock copolymer for the combination of Non with poly(2-methyl-2-oxazoline), referred to hereafter as Me. The E_r of the MeNonMe triblock copolymer is found between that of the Me homopolymer and the MeNon diblock copolymer. Likewise, for the combination of Non with poly(2-ethyl-2-oxazoline), or Et, the E_r of EtNonEt is between that of Et and EtNon (Fig. 1b). For the combinations of poly(2-phenyl-2-oxazoline), or Phe, the E_r of PheNonPhe is between that of Phe and PheNon (and NonPhe), while the E_r of NonPheNon is between that of NonPhe and Non.[23]

For the Me–Non and Phe–Non combinations, the stiffness of the AB and BA materials differ to some extent. The higher stiffness of NonMe compared to MeNon is partly attributable to the higher overall Me content. Furthermore, for the copolymers containing Non as the first block, side-reactions (chain-transfer and subsequent chain coupling) occurred.[4] Due to these side-reactions, apart from the desired AB block architecture, some ABA triblock copolymers with Non blocks at the extremities were also formed. The presence of these impurities and the slightly different chemical composition resulted in somewhat different phase-segregation and crystallization behavior during sample preparation for this material compared to its BA counterpart, causing the differences in stiffness. This is in line with the differences in surface morphology (AFM) between the NonMe and MeNon diblocks[24] and in phase behavior, as evidenced by DSC, which exhibited slightly different T_m for the AB and BA combinations.

The relation between weight fraction Non and E_r deviates from linearity for the Me–Non and Phe–Non combinations (Fig. 1a and 1c), but is nearly linear for the Et–Non combinations (Fig. 1b). The exact variation of E_r with composition for each of these series depends on various factors such as the volume fractions and stiffness of the amorphous and crystalline phase. Moreover, especially for the amorphous phase, the stiffness may vary with the chemical composition of the phase and with the amount of absorbed moisture.

Both indenter geometries yielded the same trends in material stiffness as a function of chemical composition (Fig. 1a–c). The material stiffness of Me and Et, and to a lesser extent the stiffness of Non and Phe, decreases with increasing humidity,[12] as also observed here by the significant difference between the E_r of Et at 9% and 5.4% relative humidity. The differences in magnitude of Er cannot be attributed solely to the differences in humidity. Thus, we attribute part of the discrepancy between the stiffness obtained from Berkovich and spherical indentation to the different loading times and strain magnitudes/gradients specific to each probe geometry. (The so-called representative strain can be estimated for the spherical probe, given the maximum indentation depth and probe radius,[25] and ranged 6–13% for the stiffest and most compliant polymers, respectively; the representative strain for the Berkovich probe is estimated as 8%,[25] but this probe also induced a much sharper strain gradient within the polymer). Potential geometric imperfections or inaccuracies of the empirically obtained indenter area function contribute additional sources of error to the calculated values of E_r for each probe type.

The Et–Phe combinations (Fig. 2) span a smaller E_r range than the Non-containing combinations, as the difference between the stiffness of the homopolymers is smaller. Again the E_r of EtPheEt falls between the diblock copolymer and the homopolymer. The PheEtPhe as measured with the spherical indenter[26] is less stiff than both EtPhe and PheEt, which may be attributed to some variation in the humidity during testing; an

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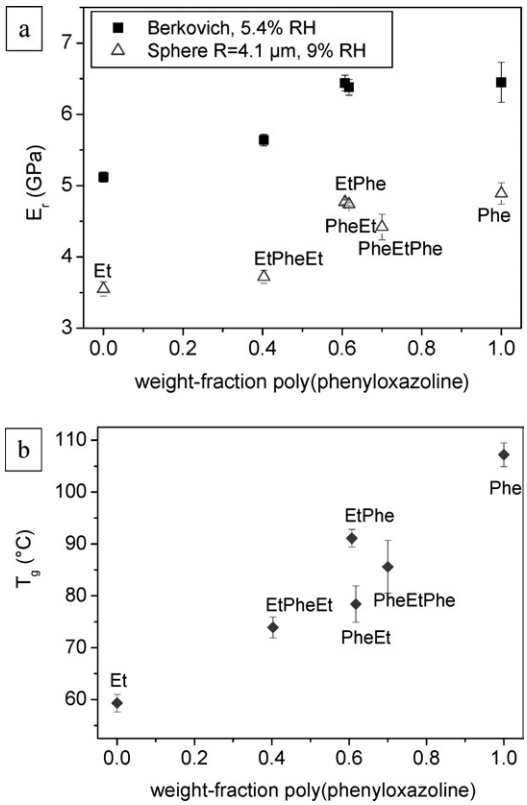

Fig. 2 (a) Stiffness of the homopolymers, diblock and triblock copolymers for the Et–Phe combinations, measured using a spherical or a Berkovich indenter at reduced relative humidity, RH, and (b) their glass transitions as obtained with DSC (DSC according to ref. 4 and 5).

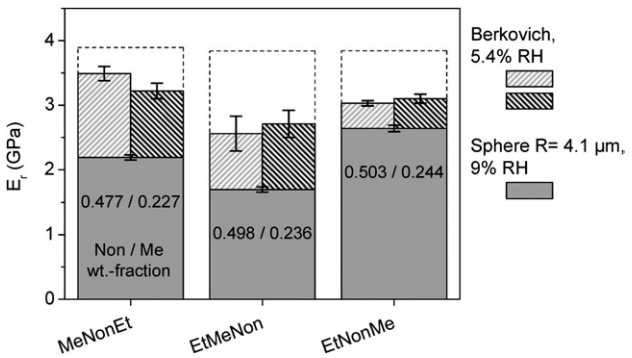

Fig. 3 E_r obtained for the Me–Et–Non triblock combinations with two different indenter geometries. The corresponding weight-averaged E_r of the homopolymers (Berkovich, 5.4% RH) is indicated by a dashed bar.

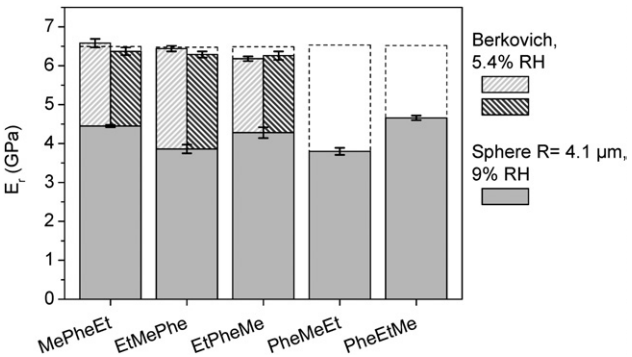

Fig. 4 E_r for the Me–Et–Phe triblock combinations. The dashed bars indicate the applicable weight-averaged E_r of the homopolymers for indentations using a Berkovich indenter at 5.4% RH.

increase in humidity would result in a decrease of the E_r of the humidity-sensitive Et block.[12] The relatively low E_r of the Et homopolymer is related to the moderate difference between the T_g of Et (59 °C) and the measurement temperature (~23 °C).[12] At 9% RH, and possibly even at 5.4% RH, some moisture is absorbed from the surrounding atmosphere, albeit only a small amount,[27] resulting in softening of the Et-material. With increasing amount of Phe, the T_g of the copolymer material increases. The material also turns less hygroscopic and, thus, the humidity-induced softening is less pronounced, as well. These two factors cause an increase of the material stiffness with increasing Phe content (Fig. 2).

Apart from the combinations of two different monomers, the triblock copolymer library contained combinations of three different poly(2-oxazoline) blocks. The material stiffness for the Me–Et–Non and Me–Et–Phe combinations are shown in Fig. 3 and 4, respectively. Also the appropriate weight-averages of the stiffness of the homopolymers are shown (dashed bars in Fig. 3 and 4) for the series measured at 5.4% RH with a Berkovich probe. These weight-averages are based on the degrees of polymerization determined by ^{1}H-NMR analysis. The E_r of the Me–Et–Non triblock copolymers is lower than the applicable weight-averaged stiffness, which is related to the observed concave trend in Fig. 1a (where the MeNonMe copolymer also exhibited a lower E_r than expected from the applicable weight average of the E_r of the Me and Non). We note that the observed differences between the stiffness of MeNonEt, EtMeNon and EtNonMe are larger than those between their respective weight-averaged stiffness (dashed bars). The higher E_r of MeNonEt compared to EtMeNon and EtNonMe (Fig. 3) is at least partly attributable to its Non content, as a lower Non content results in a higher E_r (Fig. 1). This higher E_r is more observable for the measurements with the Berkovich indenter (results obtained on both duplicate sample slides are shown in Fig. 3), as the humidity was controlled more precisely in these experiments. The Non and Me contents are annotated in Fig. 3, for clarity with one more decimal place than actually justified based on the accuracy of the NMR-analysis. We observe some difference between the E_r of EtNonMe compared to EtMeNon. This difference, which is not explained by their Non content, may be related to their Me content. It can be expected that a higher Me content increases E_r as the stiffness of MeNonMe (Fig. 1a) is larger than that of EtNonEt (Fig. 1b) or any of the Me–Non–Et triblock combinations (Fig. 3). Indeed, EtNonMe, which has a higher Me content, exhibited a higher E_r than EtMeNon. Moreover, the tendency to phase-separate and to form a nonyl-rich crystalline phase may be influenced by this change in Me content, as the Et–Non combination exhibits less tendency to phase-separate than the Me–Non combination.[28] Finally, the location of the Non block within the chain and/or the occurrence of some chain-transfer and chain-coupling side-reactions may have influenced

the crystallization kinetics and thus the resulting phase morphology (domain size, degree of crystallinity, exact composition of the phases, macromolecules connecting different amorphous domains and thereby increasing the resistance to deformation) and may have contributed to the higher stiffness observed for MeNonEt and EtNonMe compared to EtMeNon. We conclude that the relation between chemical composition on one hand, and phase-separation behavior and stiffness on the other hand, is much more complicated than can be covered by a simple weight-averaging of the stiffness of the constituent homopolymers.

The E_r of the Me–Et–Phe combinations (Fig. 4) is, in particular for the Berkovich series, relatively close to the appropriate weight averages of the E_r of the corresponding homopolymers. This straightforward relation may be related to the simple phase-behavior of the system: only one T_g is observed for these triblocks, indicating that no phase-separation occurs. Moreover, we observed only small variation in E_r between the different Me–Et–Phe triblock combinations, in particular for the Berkovich series. The difference between the highest E_r obtained on one of the duplicate samples with a Berkovich on MePheEt and the lowest obtained on EtPheMe is 0.4 GPa, which is only 6% difference. The slightly larger variation in the data obtained with the spherical indenter is attributable to some variation in drying conditions before, and relative humidity during, these indentation measurements, as the E_r of Me and of Et is sensitive to humidity.[12]

Surface energies and morphologies

The surface energies (SE) of the synthesized triblocks were calculated from the contact angles of two test liquids on spin-coated films[13] using Neumann's equation of state.[19] All triblocks without a Non block had a surface energy of ~45 mN m^{-1} (Fig. 5a). The high SE of the triblock copolymers without any Non is in line with the SE measured for the corresponding homopolymers.[13] That study also showed for Non and Non-containing diblock copoly(2-oxazoline)s a surface energy of 19 to 23 mN m^{-1}, indicating that for diblock copolymers with a Non block, this Non block segregates to the surface. Supporting evidence for this segregation of nonyl to the surface was provided by atomic force microscopy (AFM) on spin-cast films, that demonstrated that all low surface energy homopoly(2-oxazoline)s and diblock copoly(2-oxazoline)s exhibited a higher surface roughness compared to films without any Non. This higher roughness could be attributed to crystallization of the nonyl side-chains at the surface.[24] This segregation of the alkyl side-chains to the surface is in line with angle-profiling electron spectroscopy chemical analysis (ESCA) studies by Cai *et al.*[14] They observed that the alkyl side-chains of

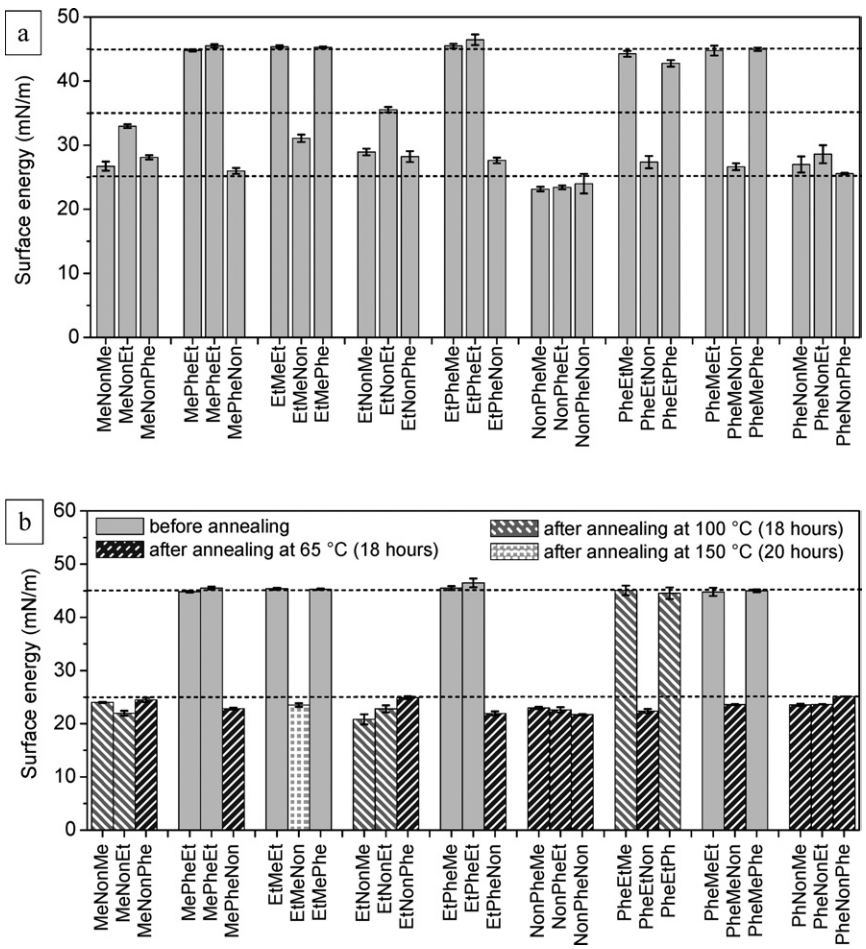

Fig. 5 Surface energies of the triblock copoly(oxazoline)s (a) after spin-coating and (b) after various annealing steps.

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poly(undecyloxazoline) oriented towards the surface, giving rise to surface energies of ~20 mN m^{-1}, while the main-chain was oriented approximately parallel to the surface. Similar surface-energies were observed for poly(*n*-alkyl methacrylates) for poly(lauryl methacrylate) and poly(stearyl methacrylate), while poly(methacrylate)s with shorter alkyl side-groups exhibited higher surface energies.[16]

For the triblocks currently studied, we observed that all triblock copolymers with a Non block combined with a Phe and/or a Me block exhibited a SE close to 25 mN m^{-1}, which is close to the SE of Non. This observation can be explained by effective phase separation between the Non and Me or Phe that facilitates preferential orientation of the nonyl side-chains towards the surface. On the other hand, the triblock copolymers that contained Non and Et blocks revealed SE values between 25 and 35 mN m^{-1}. These values are in-between the SE values of Non and Et, indicating that these blocks exhibit less surface separation due to a good miscibility of Non and Et. This good miscibility was also observed for Et–Non diblock copolymers.[28]

In order to facilitate segregation of the Non blocks to the surface, and to decrease the variation between the surface energies of triblock copolymers with corresponding compositions (in particular for the ABC, ACB, BAC, BCA, CAB and CBA triblock copolymers with one Non block, Fig. 5a), the spin-

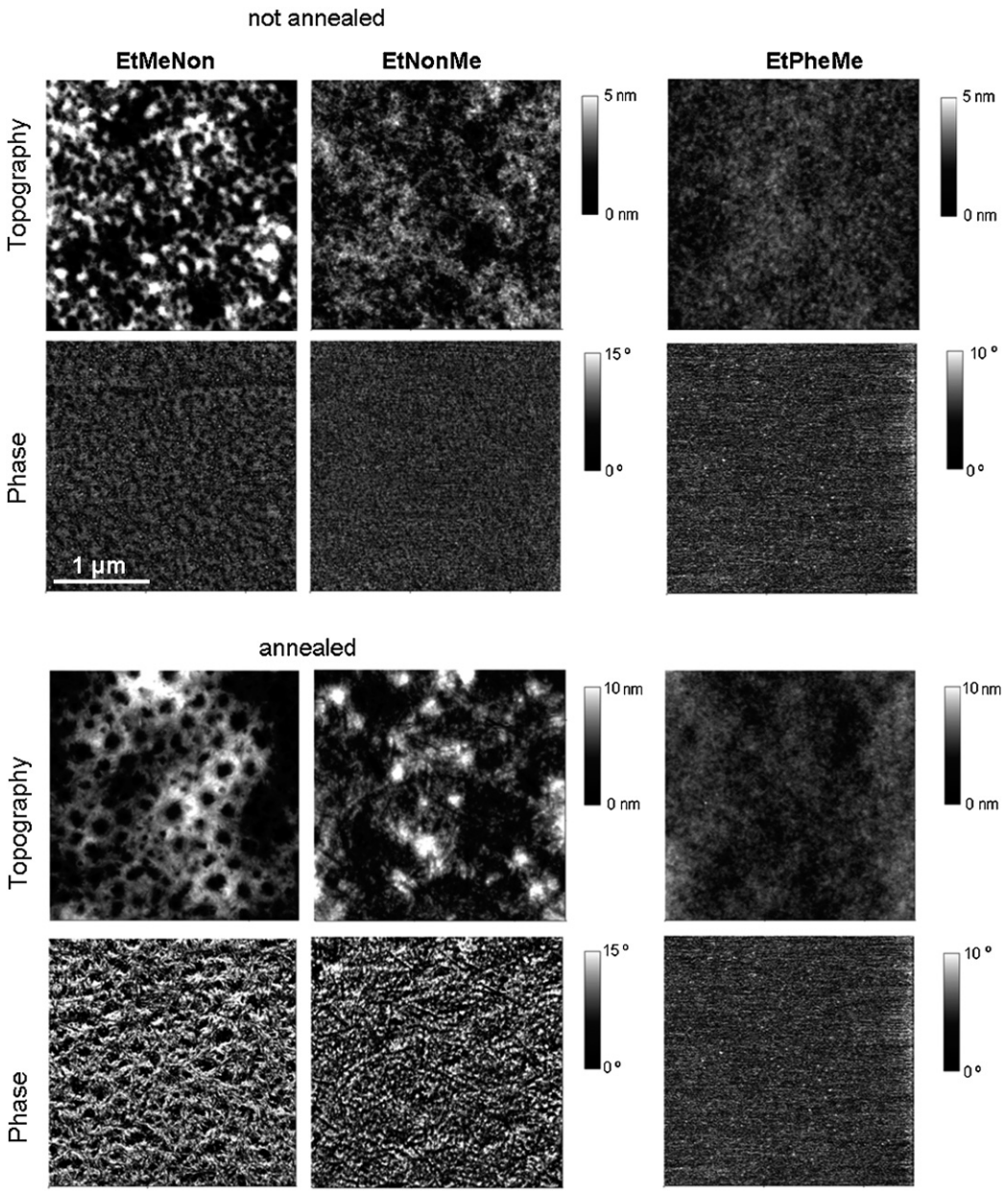

Fig. 6 Atomic force microscopy (AFM) images (2.5 × 2.5 µm) of two samples that required annealing (EtMeNon and EtNonMe) and one reference sample (EtPheMe). Topography and phase images are shown before and after annealing (for the annealing conditions, see Fig. 5). In the case of the Non-containing polymers, the surfaces are significantly roughened in the course of annealing, while the surface of the reference sample does not alter during annealing.

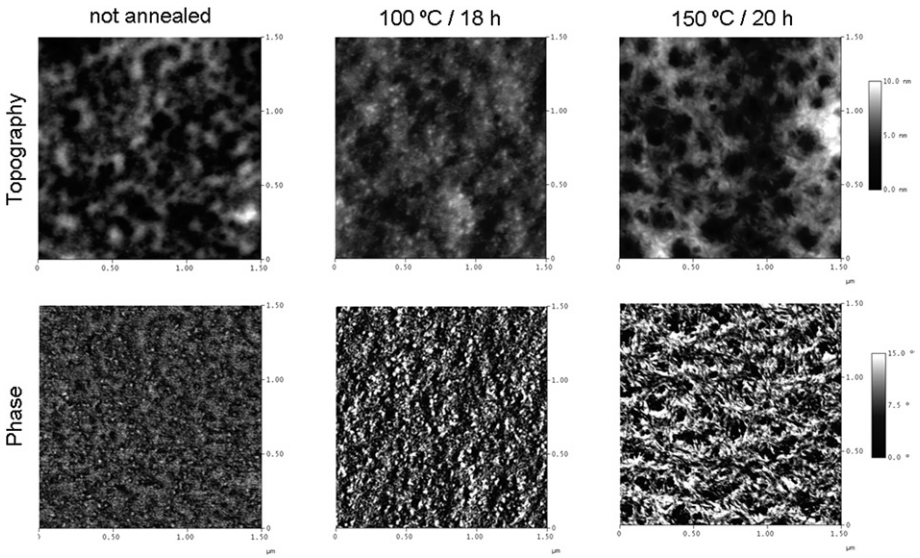

Fig. 7 Step-wise annealing of EtMeNon. Harsh annealing conditions, up to the melting point of poly(2-nonyl-2-oxazoline), were required to cause migration of Non to the film surface and subsequent crystallization, resulting in surface roughening.

coated films were annealed. Besides the Non-containing polymers, two other polymers were also annealed to verify that the SE of these polymer films did not change with annealing. After annealing at 65 °C, the SE of the triblock copolymers containing both Non and Phe decreased below 25 mN m^{-1}, indicating strong phase separation. The SE of the remaining triblock copolymers with Non as the middle block decreased below 25 mN m^{-1} after annealing at 100 °C. After this second annealing step, EtMeNon still revealed a SE of ~30 mN m^{-1}, demonstrating that also Et remained at the surface. Only melting of this polymer film at 150 °C resulted in a SE below 25 mN m^{-1}.

The difference between the results before and after annealing shows that, during spin-coating, the decrease of the mobility of the polymer segments upon evaporation of the solvent (chloroform) resulted in a non-equilibrium situation. While for the diblock copolymers with one Non block, after spin-coating low surface energies were obtained,[13] several of the triblock copolymers with one Non block displayed after spin-coating a surface energy of >25 mN m^{-1}. For the triblock materials with one Non block, the Non contents were lower (33 units compared to 50); therefore, extensive coverage of the surface with nonyl chains is achieved only at larger differences between the bulk and the surface composition. Furthermore, the blocks were shorter, resulting in a smaller driving force for phase-segregation.[29]

The surface morphology of selected spin-coated films was investigated by atomic force microscopy (AFM), before and after annealing. Annealing of EtMeNon and EtNonMe resulted in significant roughening (larger *z*-scale, Fig. 6), while the smoothness and the morphology of a reference sample, EtPheMe, remained constant. Furthermore, the triblock copolymers EtMeNon and EtNonMe showed patterned surfaces after the annealing procedure. This patterning originated from the crystallization of nonyloxazoline at the surface of the thin films. The AFM phase images after annealing show larger features for the triblock copolymer with Non as outer block compared to the triblock copolymer with Non as middle block. It is proposed that this difference is due to the easier incorporation of the outer Non block into the crystalline domains resulting in the formation of larger crystallites. Obviously, the increased temperatures, in other words, the enhanced mobility of the Non blocks in the course of the annealing facilitated the development of the surface morphologies, which was also observed by AFM monitoring of a two-step annealing process of EtMeNon (Fig. 7).

Conclusions

Elastic properties, surface energies and surface morphologies of triblock copoly(2-oxazoline)s were investigated. It was shown that the material stiffness and surface energy can be tailored by manipulating the chemical composition as well as the chain architecture. Furthermore, the smaller increments in chemical composition compared to earlier work on the corresponding homopolymers and diblock copolymers, and the different block architecture (ABA and ABC *vs.* AB), allow for a more detailed fundamental study into the parameters governing these material properties.

The stiffness of ABA triblock copolymers was in-between that of the A homopolymer and of the AB diblock copolymer. Part of the variation in E_r between corresponding ABC triblock copolymers containing Me, Et and Non could be related to variation in the chemical composition. The differences in composition resulted in slightly different phase segregation and crystallization behavior, which, subsequently, caused the variation in stiffness. The location of the Non block (middle or end block) may have influenced the resulting phase morphology, as well. The simpler phase behavior of the Me–Et–Phe system resulted in smaller variation between the stiffness of triblock copolymers with comparable composition than for the Me–Et–Non system.

The obtained surface energies and surface morphologies showed that nonyl side-chains segregate to the surface of the copolymer films, thereby reducing the surface energy. In contrast to the diblock copolymers, several triblock copolymers did not exhibit their equilibrium surface energies after spin-coating.

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However, after subsequent annealing, all of the Non-containing triblock copolymers exhibited surface energies between 21 and 24 mN m^{-1} due to the segregation of the nonyl side-chains to the surface. This segregation also resulted in crystallization at the surface and, therefore, in significant surface roughening. The annealing conditions required to reach the final low surface energy point out the good miscibility of Et and Non as compared to the combination of Me or Phe with Non. Together, these results demonstrate that the capacity to tune physical and mechanical properties of triblock polymers of this type must be tempered with direct experimental observation, as extrapolation from homopolymer phase properties will not necessarily predict the performance of the structurally complex triblock copolymer materials.

Acknowledgements

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