

Cross-Linking Induced Phase Separation in SAN/SMA Semi-interpenetrating Polymer Networks Observed by Solid State NMR and Site Specific Isotope Enrichment

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ABSTRACT: The effect of selective cross-linking of poly(styrene-*co*-maleic anhydride) (SMA) in an initially fully miscible blend with poly(styrene-*co*-acrylonitrile) (SAN) is studied as a function of cross-link density. Site specific ¹³C-enriched SMA and SAN obtained by total synthesis and CP³ magic angle spinning NMR spin diffusion techniques are used. The cross-linking of SMA results in the formation of a semi-interpenetrating network (semi-IPN) and induces phase separation. The characteristic domain sizes increase roughly linear with the amount of cross-links on a scale of 0–100 nm. The fraction of SAN and SMA that remains homogeneously mixed is also determined, and it is shown to decrease with increasing cross-link density.

Introduction

Copolymers of styrene and acrylonitrile (SAN) are miscible at the molecular level with copolymers of styrene–maleic anhydride (SMA) when the styrene contents of both copolymers are approximately equal.^{1,2} The miscibility in such SAN/SMA blends has been explained by electrostatic dipole–dipole interactions between the ACN groups of SAN and the MA groups of SMA^{3,4} or by the reduction of the intramolecular comonomer repulsion upon mixing.⁵ In a previous investigation the synthesis of respectively SAN with ¹³C labels on the nitrile and SMA with ¹³C labels on the carbonyls and on the methylene was described. ¹³C MAS NMR spin diffusion experiments with blends of these ¹³C-labeled copolymers showed that a specific orientation of the SAN nitrile moiety with respect to the SMA carbonyl moiety is unlikely.⁶

Phase separation in homogeneous SAN/SMA blends can be induced by cross-linking SMA at 50 K above the glass transition temperature (*T*_g) using a dialcohol or aromatic diamine. The onset of this phase separation at high temperature has been studied by determining the morphology of the reaction product at room temperature. At this temperature, well below the *T*_g of the blend, the mobility of both copolymers is low and the cross-linking agents are chemically inactive, the combination of which effectively inhibits progressive morphological evolution. ¹³C spin diffusion experiments with such semi-interpenetrating (semi-IPN) blends of labeled SAN and SMA clearly showed phase separation, but the domain sizes could not be quantified.⁶

The observation of structural features and distances of the order of 100 nm and less in noncrystalline, organic compounds without long-range order can be performed successfully using NMR spin diffusion techniques.^{7–13}

In principle, neutron and X-ray scattering techniques can be used for similar purposes, provided there is sufficient contrast.¹⁴ In the case of only partly demixed polymer blends this contrast will be intrinsically low. In such cases NMR can be used successfully to probe the dimensions of phase-separated regions and also the intimately mixed fraction of the material. For size ranges of ≈100 nm electron microscopy provides sufficient detail to allow a comparison with the NMR results. ¹H spin diffusion can be used for the determination of distances and morphologies if the resolution of the ¹H NMR spectra is sufficiently good. However, in rigid polymer materials the ¹H NMR resolution is generally not sufficient due to strong dipolar couplings and limited chemical shift dispersion. In blends of SMA and SAN high-resolution ¹³C NMR spectroscopy is required to discriminate between the SMA and SAN components. In this investigation we used specific ¹³C-enriched SAN and SMA polymers of which the synthesis is discussed in ref 6. The CP³ NMR spin diffusion technique using the ¹³C labels was applied that was designed for this purpose.¹⁵ Rapid ¹H spin diffusion is used to bridge distances of up to 100 nm, while the high-resolution ¹³C responses are used to select and detect polarization of ¹³C labels. SAN was ¹³C-enriched to 98% at the CN position and SMA was enriched to 98% at both the CO and the CH₂ positions. The ¹³C chemical shift of the CN label in SAN is 114 ppm, and those of the CO and CH₂ labels in SMA are 169 and 20 ppm, respectively. The clearly separated responses in the ¹³C MAS NMR spectra facilitate the discrimination between these polymers.

Materials and Methods

Materials An amount of 3.1 g of poly([β-¹³C]styrene-*co*-[1,4-¹³C₂]maleic anhydride) with 27 wt % [1,4-¹³C₂] MA (*M*_w ≈ 4 × 10⁴ g/mol) was prepared using an optimized starved feed procedure.⁶ The MA content of the copolymer is 27.0 wt %, as was determined from the ratio of the FT-IR intensities of the ¹³CO stretch absorption at 1807 cm⁻¹ and the ¹³CH₂ bend

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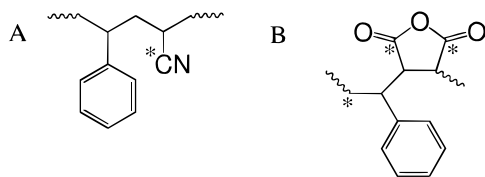


Figure 1. Chemical structure of poly(styrene-*co*-acrylonitrile) (A) and poly(styrene-*co*-maleic anhydride) (B). The asterisks indicate the positions of the ^{13}C labels.

absorption at 1493 cm^{-1} . DSC measurements were performed using a Mettler TA3000 instrument. The DSC data were collected using a heating rate of 10 K min^{-1} after annealing for 5 min at $230\text{ }^{\circ}\text{C}$. The T_g determined as the inflection point of the DSC trace was $163\text{ }^{\circ}\text{C}$, which is close to the $T_g = 162\text{ }^{\circ}\text{C}$ reported for commercial SMA with 27 wt % MA.

Poly(styrene-*co*-[^{13}C]acrylonitrile) with 27 wt % of [^{13}C]acrylonitrile ([^{13}C]SAN) was prepared as described in ref 6. The molecular weight was measured with gel permeation chromatography, $M_w = 1.3 \times 10^5\text{ g mol}^{-1}$. Using elemental C, H, and N analysis, a 27.0 wt % [^{13}C]acrylonitrile content was found. The T_g of $113\text{ }^{\circ}\text{C}$ is in good agreement with the $T_g = 112\text{ }^{\circ}\text{C}$ for commercial SAN with 27 wt % ACN. The positions of the labels in SAN and SMA are indicated schematically in Figure 1.

A 200 mg sample of [^{13}C]SAN and of [$^{13}\text{CH}_2$, ^{13}CO]SMA were codissolved in 20 mL of acetone (2.5 wt % solution) at room temperature. After the copolymers were completely dissolved, the mixture was stirred for 10 min. Subsequently, the bulk of the solvent was allowed to evaporate at ambient temperature. The blend was then dried at $50\text{ }^{\circ}\text{C}$ and at reduced pressure for at least 48 h. Semi-IPNs were prepared in a similar procedure. The 4,4'-methylenedianiline cross-linker was first dissolved in a small fraction of the acetone and added to the SMA/SAN solution. SMA was selectively cross-linked by the diamine in the SAN/SMA 50/50 blend by heating at $50\text{ }^{\circ}\text{C}$ above the T_g of the blend. When more than 4.5% cross-linker per monomer unit in SMA was added, the semi-IPNs appear phase separated as evidenced by DSC.⁶ Mixtures prepared with 1.5–3.5% diamine cross-linker give rise to thermograms indicating intermediate stages of demixing. In the following the blends are denoted by the added amount of cross-linking agent as a percentage of the MA monomer content. Note that the actual conversion of MA is probably smaller than the theoretical one.

MAS NMR Methods The MAS NMR experiments were performed at room temperature with a spinning speed of $6650 \pm 5\text{ Hz}$ using a modified Bruker 400 MHz spectrometer. The CP³ ^1H spin diffusion pulse sequence was used for the determination of the domain sizes by 2D high-resolution CP-MAS NMR correlation spectroscopy. This pulse sequence is described in detail in ref 15. In Figure 2a the pulse sequence is plotted, and the phases of the pulses are given in Table 1. After cross-polarization (CP) from ^1H , selection of the magnetization is performed for the ^{13}C isotope labels on the basis of their ^{13}C chemical shifts. Following a second Hartmann–Hahn transfer, the shift-modulated ^{13}C polarization is transferred back to the abundant ^1H , and equilibration of magnetization proceeds via genuine ^1H spin diffusion. Finally, after a third heteronuclear transfer period, the encoded information is detected with ^{13}C MAS NMR. The method combines the high resolution of ^{13}C MAS for selection and detection with the efficient polarization transfer via strong ^1H dipolar interactions.

A 1D version using DANTE spectral editing allows for improved efficiency with respect to measurement time and was applied for the majority of the measurements (Figure 2b). Here a rotor synchronized DANTE^{16,17} pulse sequence was used to reverse the ^{13}C magnetization on the CN label of SAN. The integrated intensity I_{CN} of the ^{13}C MAS response of SAN was normalized relative to the saturation value $I_{\text{CN}}^{\text{sat}}$, and I_{CN} was also corrected for the T_1 relaxation of ^1H during the spin diffusion time t_m . This yields $\hat{I}_{\text{CN}} = [I_{\text{CN}} \exp(t_m/T_1) + I_{\text{CN}}^{\text{sat}}]/2I_{\text{CN}}^{\text{sat}}$.

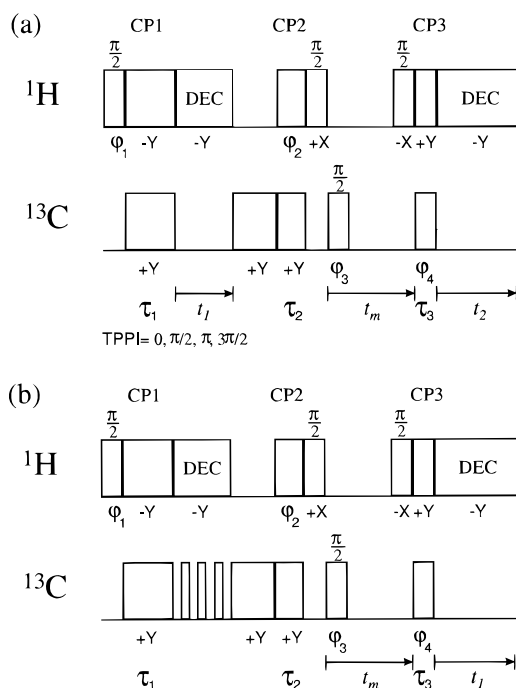


Figure 2. CP³ NMR pulse sequences for probing ^1H spin diffusion with ^{13}C selection and detection, using 2-D ^{13}C – ^{13}C correlation spectroscopy (a) and using 1-D inversion recovery experiment including a selective rotor-synchronized DANTE inversion period (b).

Table 1. Phases of the NMR Pulses in the CP³ Pulse Sequence As Defined in Figure 2; A Full Cycle of the Sequence Is Four Scans

scan	ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_{rec}
1	$+X$	$-Y$	$-X$	$+Y$	$-X$
2	$+X$	$+Y$	$-X$	$-Y$	$-X$
3	$-X$	$-Y$	$+X$	$+Y$	$+X$
4	$-X$	$+Y$	$+X$	$-Y$	$+X$

The use of CP³ makes that the method is most suitable for rigid polymers, well below their glass transition temperatures, as is the case for these SAN and SMA blends. For other polymeric materials with unresolved ^1H signals, but sufficient differences in the polymer chain dynamics, techniques using dipolar filters may be more readily applicable.^{18,19} The reason for that is that the differences in polymer mobility will influence the CP efficiencies in such a way that the mobile fractions of the material become relatively (much) less visible²⁰ using CP³. In the present investigation both SAN and SMA are rigid, however, which makes that CP³ is the technique of choice; the dipolar filter techniques cannot be applied since there is not sufficient difference between the ^1H homonuclear dipolar interactions in SAN and SMA.

Additional Characterization. The 50% blend used for the NMR experiments was examined afterward with TEM in order to verify the domain size found in the NMR analysis. A dispersion of the blend in an epoxy resin was cured, and 70 nm coupes were cut at room temperature. To obtain contrast, it was necessary to wash the blend surface with MEK, which dissolves the SAN and leaves the cross-linked SMA structure intact. After 15 min etching with methyl ethyl ketone (MEK) the coupes were washed with water and dried in air. Micrographs were recorded with a Philips CM200 TEM (120 kV). For the blends with lower amounts of cross-links the domain sizes were too small to be resolved clearly by TEM.

Results and Discussion

Figure 3 shows the 2D ^{13}C NMR correlation spectra collected for a 35% blend. The two spectra have ^1H spin diffusion times of $t_m = 0$ and 40 ms, respectively. Each

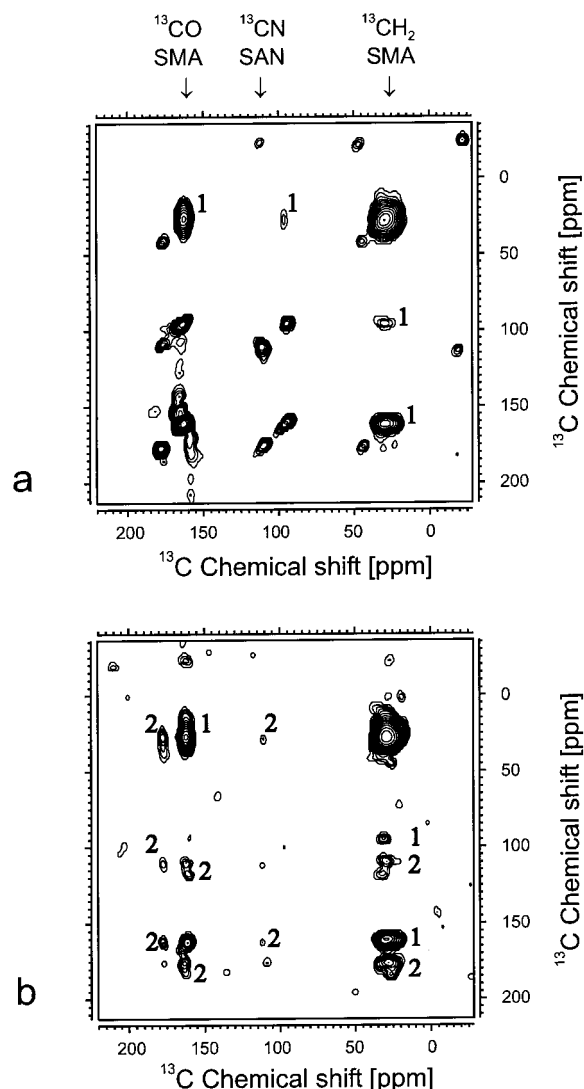


Figure 3. 2-D ^{13}C – ^{13}C NMR correlation spectra of the phase separated semi-interpenetrating network of selectively ^{13}C labeled SAN and SMA (50/50; w/w) with 35% cross-linker. The measurements used durations τ_1 , τ_2 , and τ_3 of 2, 1, and 1 ms, respectively. The spin-lock time following t_1 was 400 μs , and the spinning speed was $\omega_r/2\pi = 6550 \pm 3$ Hz. (a) Data set collected with a mixing time $t_m = 0$ ms. The ^{13}CO and $^{13}\text{CH}_2$ of SMA resonate at 196 and 20 ppm, respectively. The correlations resulting from intramolecular magnetization exchange in SMA are indicated with 1. (b) $t_m = 40$ ms. The ^{13}CN peak in SAN has an isotropic chemical shift of 114 ppm, with a strong sideband at 180.5 ppm that yields the more intense interdomain correlations. They are indicated with a 2.

2D measurement requires data collection for about 20 h. The duration of the last two CP periods is 1 ms each. This is a compromise between the signal intensity (lower for shorter durations) and the effective length of the spin diffusion time (smaller offset for shorter durations). With this choice it can be concluded from the $t_m = 0$ ms spectrum that the total time of the last two CP's (2 ms) is sufficient to give strong intramolecular cross-peaks between the CO and CH₂ groups of SMA. This may be expected since the average distance between these labels is 3.0 ± 0.1 Å. The result indicates that the pulse sequence for $t_m = 0$ ms makes these short distances observable. This contrasts with the ^1H driven ^{13}C spin diffusion experiments in ref 6 where a mixing time of at least 50 ms was required to reveal these cross-peaks. To study the intimately mixed fraction in more detail,

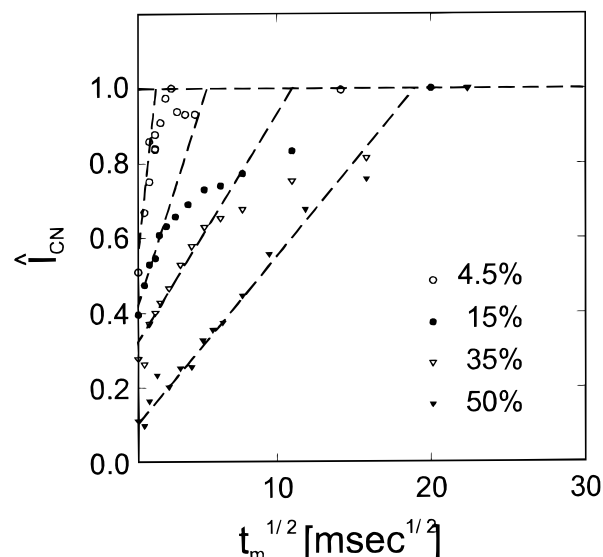


Figure 4. Intensity \hat{I}_{CN} of the CN sideband pattern of ^{13}C -labeled SAN versus the square root of the mixing time t_m . The numbers indicate the amount of 4,4'-methylenedianiline cross-linker added as a percentage of the amount of MA monomers in the blend. As described in refs 12 and 15, the point at $t_m = t_m^*$ in which the dashed lines cross determines the characteristic phase separated domain size d .

shorter CP times than 2 ms should be used while maintaining good signal intensity. Methods suppressing the homonuclear dipolar interaction during cross-polarization are required then. This could be realized by Lee–Goldburg²¹ or by windowless isotropic mixing (WIM) techniques.²²

For the longer spin diffusion time of 40 ms the spectrum shows clear cross-peaks between the site specific ^{13}C -labeled CN group of SAN and the site specific ^{13}C -labeled CH₂ and CO groups of SMA (Figure 3b). This demonstrates that there is a substantial intermolecular polarization transfer across domain boundaries, which could not be observed using the techniques in ref 6. It illustrates the much larger length range that has become accessible using the pulse sequence in Figure 2.

In Figure 4 the normalized intensities \hat{I}_{CN} of the CN responses, extracted from the measurements of the different blends using the 1D pulse program, are plotted versus the square root of the mixing time $t_m^{1/2}$. The zero in the vertical scale indicates complete reversal of the signal, while unity corresponds to full relaxation to the equilibrium. Every experimental data point in Figure 4 represents 4 h of measurement time (8000 scans). For most blends there is considerable polarization transfer already for $t_m = 0$ ms (total inversion of the ^{13}CN signal). This is ascribed to spin diffusion between SAN and SMA occurring during the last two heteronuclear Hartmann–Hahn periods in the interphase, which is the most intimately mixed fraction of the polymers. These two periods are 2 ms in total, which apparently is sufficient to homogenize the magnetization in the fraction of the blend that is intimately mixed. In Figure 5 this fraction of the various blends is plotted versus the amount of 4,4'-methylenedianiline cross-linking agent added. From the study in ref 6 we learned already that a substantial fraction of the material remained intimately mixed upon cross-linking. In contrast to the present investigation, these ^{13}C spin diffusion experiments yielded no quantitative information about the relative amount of material that was involved.

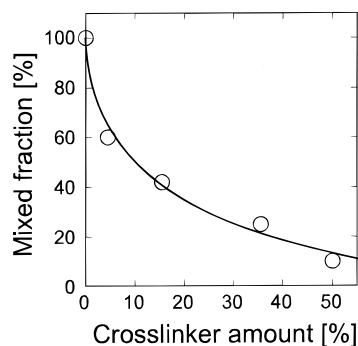


Figure 5. Molecularly mixed fraction of the SAN/SMA blend plotted versus the amount of 4,4'-methylenedianiline cross-linker as determined by spin diffusion experiments. The line is a guide to the eye.

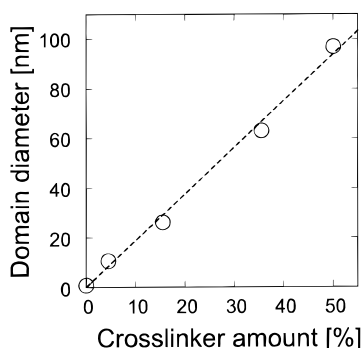


Figure 6. Domain size d versus the amount of 4,4'-methylenedianiline cross-linker in SAN/SMA semi-interpenetrating networks as determined by spin diffusion experiments.

In the model for spin diffusion analysis described in ref 13, the characteristic domain size d is defined as the diameter of a spherical domain of either type of the two polymers in the blend. The description in terms of a spherical domain will be a good approximation since domains will be formed that can have spin diffusion across its boundaries in close to three mutually perpendicular directions. The NMR results using this approximation will appear below to be consistent with electron microscopy. In the analysis for each of the blends, the line with the slope of the first points in Figure 4 crosses the saturation level 1, in the point defined as $t_m = t_m^*$. The expression $d = 6(4Dt_m^*/\pi)^{1/2}$ yields the characteristic domain sizes d . A spin diffusion coefficient $D = 0.7 \pm 0.1 \text{ nm}^2 \text{ ms}^{-1}$ is used, which is considered a normal value for these materials.¹³ This value of D is used for both SAN and SMA since both polymers are rigid at room temperature and have similar ^1H densities. The spinning speed used is not very high (6550 Hz) and has no large influence on the width of the ^1H MAS spectra, so the influence of MAS on the ^1H dipolar couplings and D is limited. The error bars for the domain size d obtained are intrinsically large, since there will be a certain distribution in actual domain sizes. In Figure 6 the domain sizes are plotted versus the amount of cross-linking agent added. There appears to be an approximately linear dependence, at least in the range $1 < d < 10^2 \text{ nm}$.

The domain size obtained from spin diffusion in the 50% semi-IPN is sufficiently large to be observed by TEM as is displayed in Figure 7. A typical semi-IPN morphology is observed, with both dark continuous SMA and light (holes) continuous SAN phases. The length scales (50–100 nm) observed from the picture compare favorably with the domain size from the NMR spin

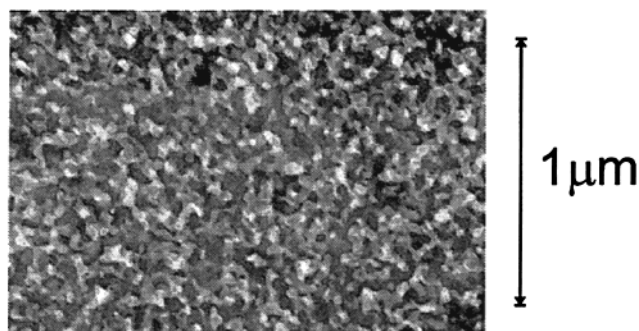


Figure 7. TEM micrograph of the 50% SAN/SMA semi-interpenetrating network. The SAN phase has been dissolved by treatment with MEK, revealing the SMA network structure.

diffusion experiments. This validates the NMR procedure for domain size determination and confirms the value of the spin diffusion coefficient D that was used in the analysis. Extraction of a 50% semi-IPN with MEK yielded a residue of 64 wt %, which according to FT-IR still contained SAN (as determined from the $^{13}\text{C}\equiv\text{N}$ absorption at 2190 cm^{-1}). This shows that SAN, although it is not chemically linked to the SMA network, is still partly intimately mixed with SMA and thus shielded from MEK extraction.

The actual cross-link density of the SAN/SMA blends is determined by the amount of cross-linker added as well as the curing time at high temperature. The curing time dependence was obtained by performing IR absorption measurements on the 25% semi-IPN. The cross-linking reaction can be followed by the conversion of the anhydride into the imide. As a result of the ^{13}C labeling, the characteristic anhydride and imide $\text{C}=\text{O}$ peaks have shifted from 1860/1780 to 1805/1735 cm^{-1} and from 1780/1710 to 1735/1665 cm^{-1} , respectively. Increasing the curing time at 230 °C from 0 to 20 min shows an increasing conversion with a maximum conversion of MA groups of $\approx 30\%$. This shows that with the 5 min curing time that was used for all blends investigated by NMR we observed the effects of cross-linking, at a moment in the process before saturation of the amount of cross-links. The cross-link density of the NMR samples will then be proportional to the amount of cross-linking agent added. Figure 6 can therefore also be interpreted as an approximately linear dependence of the domain size d on the number of cross-links in SMA.

The evolution of the morphology upon cross-linking is a complex phenomenon that will be determined by several factors. At elevated temperatures these factors are for example the amount of the cross-linking agent, the cross-linking rate, the diffusion rate of SAN through the increasingly cross-linked and immobilized SMA, and entropic factors of SAN that can choose between different mesh sizes in the SMA matrix. For example, if the cross-linking rate is extremely high, the homogeneous SAN/SMA system would have been fixated. If, on the other hand, the cross-linking rate is slow compared to the demixing process, a very coarse demixed system would have resulted. Our experimental results show that the balance of these factors in the SAN/SMA blends in the initial stage of phase separation on a length scale up to 100 nm yields a more or less linear correspondence between the cross-link density and the characteristic domain size. This also indicates that there is a means of control over morphological evolution in this small size range.

Conclusions

The effect of selective cross-linking of SMA in homogeneous SAN/SMA blends was studied. Using site specific enriched SAN and SMA polymers in combination with a recently developed NMR technique, the characteristic scale of the blend morphology was determined on a microscopic level. An approximately linear dependence of the induced domain sizes on the amount of cross-linker was found. An increasing fraction of the blend becomes demixed upon increasing the amount of cross-linker.

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