# Investigation of phase structures and intermolecular interactions of nylon-11/polyepichlorohydrin blends

**Xiaoqing Zhang*†, Masahiko Shimoda and Akinobu Toyoda***
*Analytical Chemistry Group, Research and Development Centre, Nippon Zeon Co. Ltd, 1-2-1 Yako, Kawasaki-ku, Kawasaki 210, Japan*
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Phase structures of nylon-11/polyepichlorohydrin (Ny-11/PECH) blends are studied by nuclear magnetic resonance, differential scanning calorimetry and transmission electron microscopy techniques. In the solid state, although the domain size of these mechanical blends is 1–2 $\mu$m, blending does change the motional states/phase structures of the two components. The motional freedom of PECH chains decreases as the composition of Ny-11 increases in the blends. The amorphous phase of Ny-11 changes less after blending, but increasing PECH in the blends causes the crystalline phase of Ny-11 to be disordered and the crystallinity of Ny-11 component to decrease. When the blend is PECH-rich, the crystalline phase of Ny-11 component disappears. The two-dimensional nuclear Overhauser effect result indicates that there are intermolecular interactions between Ny-11 and linear PECH chains, and the system is miscible in dimethylsulfoxide solution.

**(Keywords: nylon-11; polyepichlorohydrin; intermolecular interaction)**

## INTRODUCTION

Nylons (polyamides) are crystalline polymers that have excellent properties, such as toughness, rigidity, wear resistance, corrosion resistance and so on, for common applications. The impact property of nylons can be improved by blending with an elastomer as a dispersed phase. Recent reports[1–5] of nylon–rubber systems showed that, although these systems are usually immiscible on small scales, the mechanical properties of the materials can be improved greatly. Since the physical properties of the polymers are closely related to the phase structures, it is very interesting to study the intermolecular interaction and phase structures of the blends.

Nuclear magnetic resonance (n.m.r.) methods, together with transmission electron microscopy (TEM) and differential scanning calorimetry (d.s.c.), are carried out for the study of nylon-11/polyepichlorohydrin (Ny-11/PECH) blends. Both polymers contain dipolar atoms and groups such as oxygen, chlorine, C=O and NH. Intermolecular interactions could occur between the two polymers. The PECH rubber used here is crosslinked with a crosslink density of 2 mol%, since common rubbers in applications are usually crosslinked. It was suggested that slightly crosslinked rubber is a little more effective as an impact modifier for plastic than uncrosslinked[6]. In addition, the crosslinks change the viscosity of the rubber, and affect the blending process and the rubber domain size, thus strongly influencing the impact behaviour of the blends[7]. Solid-state n.m.r. provides a valuable tool to study multicomponent polymers[8–11]. Various $^1$H and $^{13}$C parameters provide information on chemical structures and molecular motions of polymer systems, and thus the intermolecular interaction, miscibility and phase structures of polymer blends can be studied in detail. Recent reports have also shown that the two-dimensional nuclear Overhauser effect measurement (2D-NOE) is powerful to examine specific intermolecular interactions of polymer blends in the solution state[12–17]. Various n.m.r. observations, such as 2D-NOE, $^1$H broad-line n.m.r. and $^{13}$C high-resolution solid-state n.m.r., are applied in this study. The phase structures of the two components and intermolecular interactions between the two polymers in both the solution state and the solid state are examined.

## EXPERIMENTAL

### *Sample preparation*

Ny-11 (Rilsan B) with molecular weight of 26000 was produced by Atochimie Co. Ltd. PECH (Gechron 1000) was produced by Nippon Zeon Co. Ltd. Its molecular weight is 500000.

The PECH used in the blends was crosslinked (2 mol%) by a thiol compound as a crosslink reagent. The crosslinking was performed at 160°C for 30 min. The crosslink density was evaluated by the swelling equilibrium method. Ny-11/PECH blends were prepared by melt mixing in a Brabender at 190°C according to compositions shown in *Table 1*. The residence time was 20 min and the rate of rotation was 80 rev min$^{-1}$. Then, the melt blending samples were quenched by water, and dried at 70°C under reduced pressure for 16 h.

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* To either of whom correspondence should be addressed
† Present address: School of Chemistry, The University of Melbourne, Parkville, VIC 3052, Australia

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### *TEM, d.s.c. and n.m.r. experiments*

TEM results were observed on a JEOL EM-1200EX transmission electron microscope. Test specimens of Ny-11/PECH blends were sliced into thin sections of 10 nm thickness by a cryo-ultramicrotome (Reichert-Jung Optische werke AG, Austria). D.s.c. measurements were carried out on a Seiko RDS 220 DSC apparatus, and made on ca. 5.5 mg samples after quick cooling following the first heating scan. The scanning rate was 10°C $\mathrm{min}^{-1}$ within a temperature range of $-100$ to $+250$°C.

$^1$H spin–spin ($T_2$) and spin–lattice ($T_1$) relaxation times were measured on a Bruker Minispec PC-120 broad-line n.m.r. spectrometer at 20 MHz for protons, by solid-echo (echo delay of 8 $\mu$s) and inversion-recovery (180°—$\tau$—90°) pulse sequences, respectively. The 90° pulse width was 2 $\mu$s. Solid-state high-resolution $^{13}$C n.m.r. experiments were carried out on a JEOL JNM-EX270 spectrometer at 270 MHz for $^1$H and 67.8 MHz for $^{13}$C under conditions of magic-angle sample spinning (m.a.s.) and high-power decoupling. The radiofrequency (r.f.) field strengths for both $^1$H and $^{13}$C were about 60 kHz. The solid-state $^{13}$C spectrum of Ny-11 was observed by the normal cross-polarization (c.p.) pulse sequence with a contact time of 1.2 ms, while those of PECH and Ny-11/PECH blends were observed by pulse saturation transfer (p.s.t.) method[18], in which the $^{13}$C magnetization was enhanced by nuclear Overhauser effect (NOE). The rate of m.a.s. was 5 kHz in all cases. The chemical shift of $^{13}$C was determined by taking the methine carbon resonance of solid adamantane (29.5 ppm) as an external reference standard. The Torchia pulse sequence[19] was used to measure $^{13}$C $T_1$ values of Ny-11 and to describe the $^{13}$C magnetization of the crystalline phase of Ny-11 component by $^{13}$C $T_1$ difference.

**Table 1** Compositions of Ny-11/PECH blends

| Sample | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Ny-11/PECH (wt%) | 100/0 | 75/25 | 50/50 | 25/75 | 0/100 |
| Ny-11/PECH ($^1$H %) | 100/0 | 86/14 | 68/32 | 41/59 | 0/100 |

The Ny-11/PECH sample for solution n.m.r. study was prepared by mixing Ny-11 and linear PECH in the ratio of 1/4 by weight in deuterated dimethylsulfoxide (99.8% DMSO-$d_6$) solution. The concentration of polymer solution was 10 wt%. In order to achieve complete mixing, the solution was stirred for 20 h at 100°C, and then kept for two weeks at room temperature. The 2D-NOE (NOESY) spectrum was acquired by the 90°—$t_1$—90°—$t_m$—90°—$t_2$ pulse sequence on a JEOL JNM-GX500 spectrometer at 500 MHz for protons. The 90° pulse width was 13 $\mu$s and the step of $t_1$ and $t_2$ was 0.5 ms. The spectrum was taken with a total of 256 complex spectra and each containing 2048 points with 64 scans. Mixing time $t_m$ was set in the range of 10–500 ms. Tetramethylsilane (TMS) was used as an internal chemical shift reference. Temperature was controlled within $\pm 1$ K using a JEOL temperature controller.

## RESULTS AND DISCUSSION

Ny-11/PECH samples studied here are mechanical blends and the PECH is slightly crosslinked. The TEM micrographs (shown in *Figure 1*) show phase heterogeneity in the blends. The size of uniformly distributed domains is 1–2 $\mu$m for all compositions studied. *Figure 2* shows the d.s.c. curves of Ny-11/PECH blends. The glass transition temperature ($T_g$) of the blends and the melting temperature ($T_m$) of the crystalline Ny-11 in the blends are listed in *Table 2*. The pure 2 mol% crosslinked PECH shows an apparent $T_g$ at $-18$°C, and the transition range is narrow, i.e. $\Delta T_g$ is just 6°C. For semicrystalline Ny-11, a broad $T_g$ was found at 45°C, which is consistent with the value previously reported[20]. Two sharp melting endothermic peaks at 178 and 188°C were observed for pure Ny-11 corresponding to $\alpha$ and $\delta$ crystal forms of Ny-11 crystalline phase. After blending, the $T_g$ value of PECH component shows less change and the $\Delta T_g$ is around 5°C. The $T_g$ value of Ny-11 component changes less after blending. But the $T_g$ range and, moreover, the melting behaviour of the crystalline phase of Ny-11, are much different after blending. When the blend is rich in

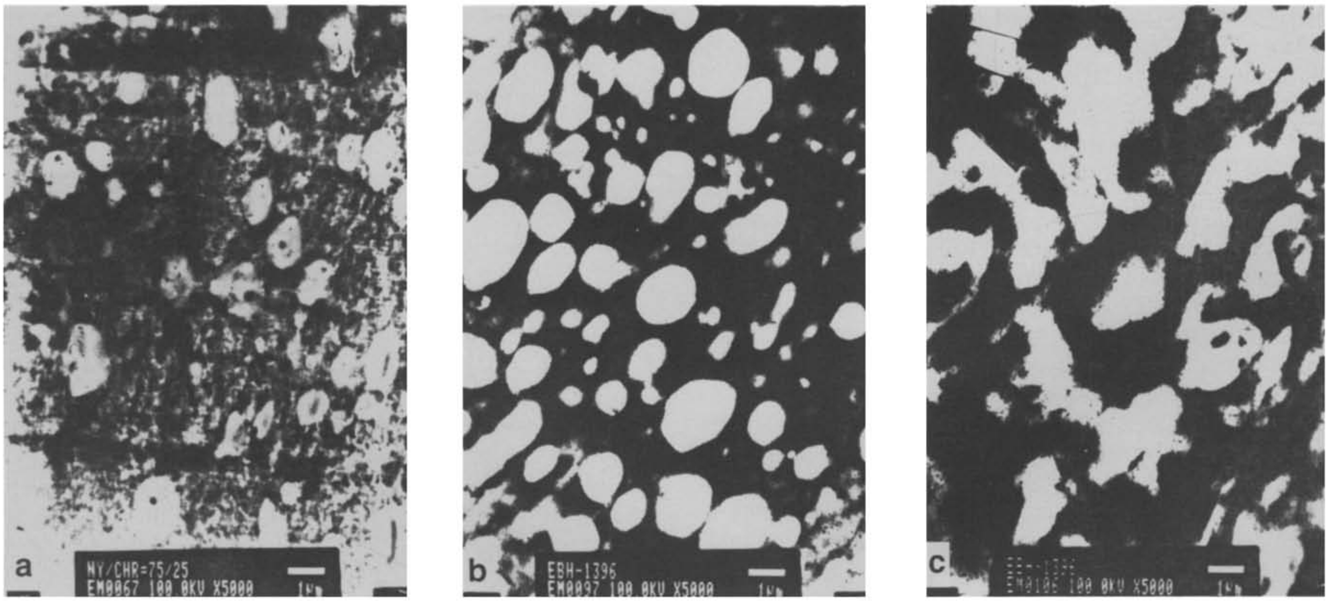

**Figure 1** TEM micrographs of Ny-11/PECH blends: (a) Ny-11/PECH = 75/25; (b) Ny-11/PECH = 50/50; (c) Ny-11/PECH = 25/75

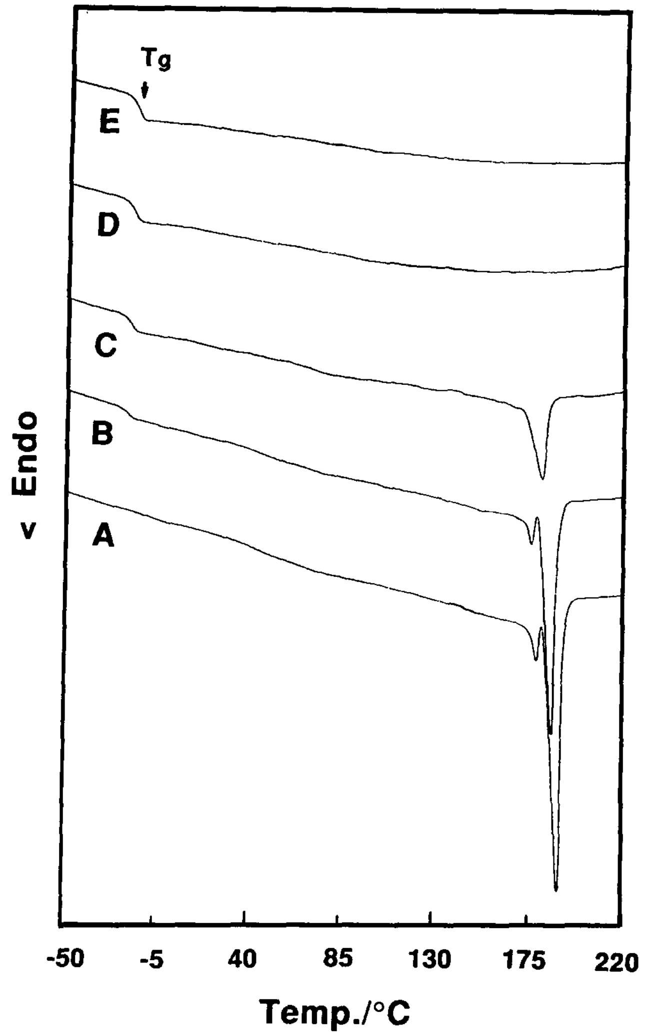

**Figure 2** D.s.c. curves for neat Ny-11 (A), Ny-11/PECH = 75/25 (B), 50/50 (C), 25/75 (D) blends and neat PECH (E)

**Table 2** The $T_g$(°C) and $T_m$(°C) of Ny-11/PECH blends

| | PECH | | Ny-11 | | | |
|---|---|---|---|---|---|---|
| Sample | $T_g$ | $\Delta T_g$ | $T_g$ | $\Delta T_g$ | $T_m$ | |
| Ny-11 | | | 45 | 25 | 178 | 188 |
| 75/25 | −20 | 5 | 45 | 16 | 177 | 186 |
| 50/50 | −19 | 5 | 48 | 13 | − | 180 |
| 25/75 | −19 | 5 | 46 | 55 | − | − |
| PECH | −18 | 6 | | | | |

Ny-11 (Ny-11/PECH = 75/25), the two $T_m$ peaks shift to lower temperature (177 and 186°C), while the $T_g$ of the amorphous Ny-11 becomes somewhat apparent. When PECH reaches 50%, the main $T_m$ peak becomes broad and shifts to 180°C, while the minor one at lower temperature tends to disappear. For the 25/75 PECH-rich blend, no $T_m$ peak can be observed for the Ny-11 component. The $T_g$ range of the amorphous Ny-11 now becomes very broad ($\Delta T_g$ of 55°C). These suggest the decrease of crystallinity of Ny-11 component after blending. This phenomenon is explicable in terms of thermodynamic mixing to a certain extent accompanied by exothermic interaction between a crystalline polymer and an amorphous polymer. Although the domain size of Ny-11/PECH blends is large, the blending effect on phase structures could be significant.

$^{13}C$ high-resolution solid-state n.m.r. spectra of neat Ny-11, PECH and their blends at 25°C are shown in *Figure 3*. The spectrum of Ny-11 was observed by the normal c.p./m.a.s. method (*Figure 4a*). Since the PECH component is mobile with a poor c.p. ability, the spectra of PECH and the blends were observed by the p.s.t./m.a.s. method (*Figure 4b*)[18]. By this method, $^{13}C$ magnetizations are induced by a single 90° pulse directly with the magnetization enhanced by saturated protons through the nuclear Overhauser effect. With $m = 500$, about 5 s repetition time, the signals observed are mainly due to the resonances in mobile phases. Resonances of PECH at 79.3, 69.8 and 44.1 ppm correspond to the CHO, $CH_2O$ and $CH_2Cl$ carbons, respectively[21]. For Ny-11, the peak at 173.2 ppm is assigned to the C=O carbon resonance, the 40.2 ppm peak to the $CH_2$ carbon directly bonded to the NH, the 36.2 ppm peak to the $CH_2$ carbon directly bonded to the C=O, the 27.2 ppm peak to the $CH_2$ carbon bonded to the $-CH_2-C=O$, and the peaks at 32.5 and 30.5 ppm correspond to the other carbons, respectively, by referring to the work on nylon-4 and nylon-6[22,23]. Comparing both chemical shifts and linewidths of the blends to those of neat polymers (*Table 3*), the changes in chemical shift are very small and most are within the measurement error. But the linewidths of both components become broader after blending. The line broadening of the resonances of the Ny-11 component is partially due to the measurement method. Resonances of amorphous Ny-11 chains should have a relatively broad linewidth at room temperature, which is easy to detect by the p.s.t. method, while the c.p. method is

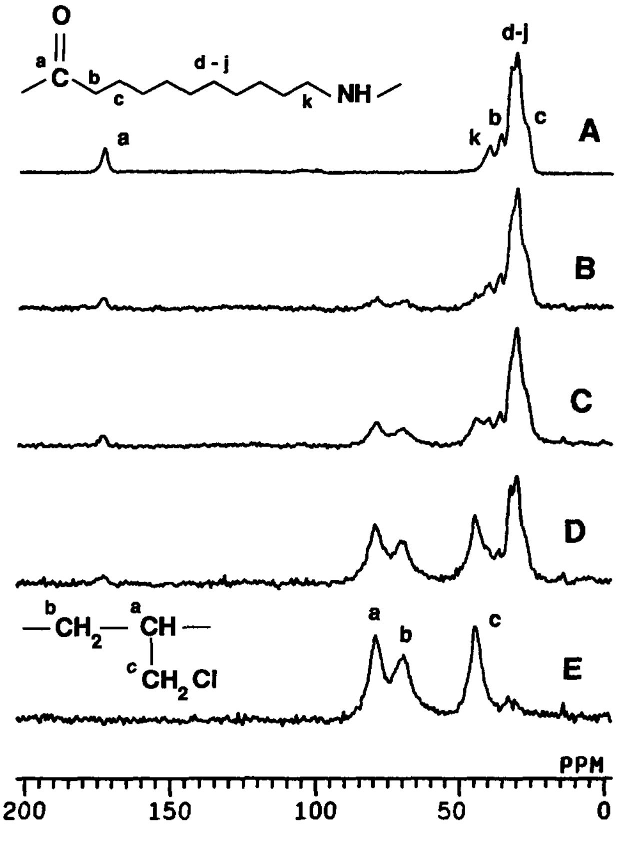

**Figure 3** The high-resolution solid-state $^{13}C$ spectra of Ny-11/PECH blends: (A) neat Ny-11; (B) Ny-11/PECH = 75/25; (C) Ny-11/PECH = 50/50; (D) Ny-11/PECH = 25/75; (E) neat PECH. (A) was observed by the c.p./m.a.s. method, and (B)–(E) were observed by the p.s.t./m.a.s. method

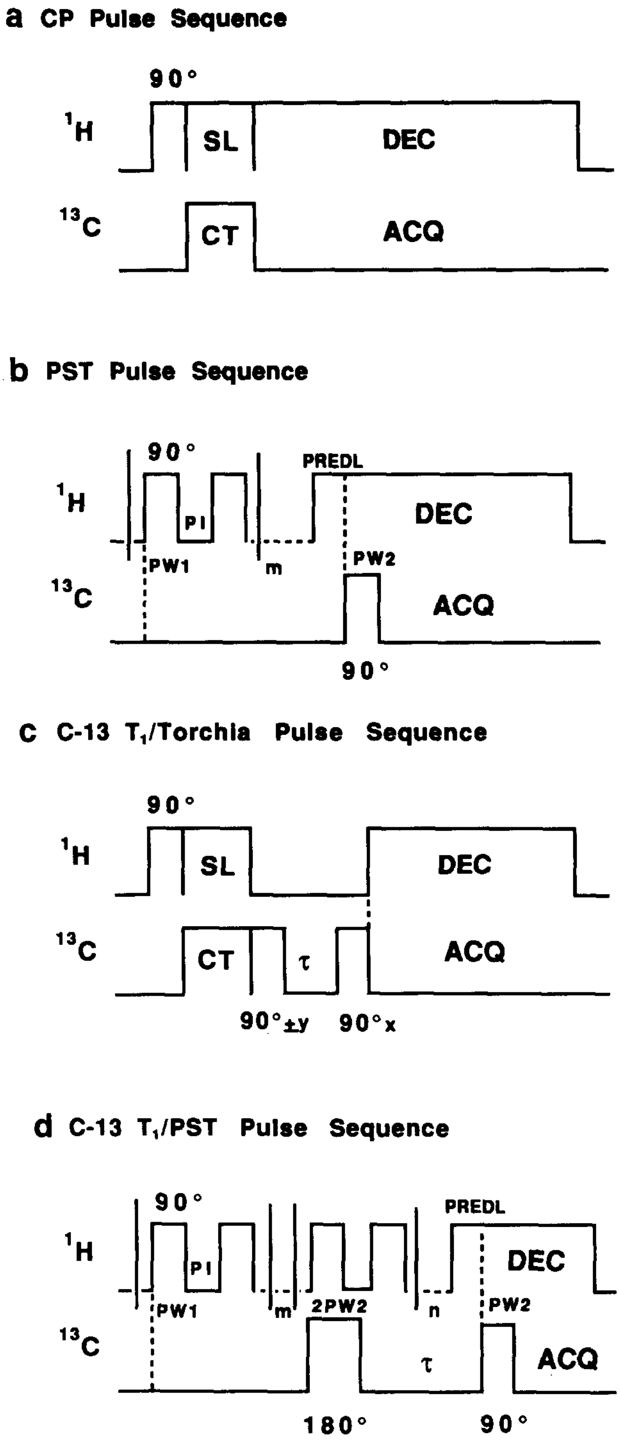

**Figure 4** Pulse sequences used in $^{13}$C solid-state high-resolution n.m.r. measurements: (a) cross-polarization (c.p.) pulse sequence, 90° pulse width for $^1$H is 5 μs; (b) p.s.t. pulse sequence, $PW1=PW2=5.5$ μs, $PI=10$ ms, $m=500$ and $PREDL=1$ ms; (c) $^{13}$C $T_1$/Torchia pulse sequence, 90° pulse width for both $^1$H and $^{13}$C is 5 μs; (d) $^{13}$C $T_1$/p.s.t. pulse sequence, parameters are the same as in (b) and $n$ is set for variable delay time

sensitive to the rigid crystalline component of Ny-11, which has a relatively narrow linewidth. The linewidth broadening of crosslinked PECH was found to be caused by the change of chemical environment, such as existence of various chemical shift structures and freezing effects in conformational environment as chain mobility decreased by crosslinking[24]. In this case, the existence of Ny-11 chains seems to cause an additional line broadening of PECH.

$^{13}$C $T_1$ values of Ny-11/PECH blends are shown in *Table 4*. The values of neat Ny-11 were observed by Torchia pulse sequence (*Figure 4c*)[19]. For pure PECH and Ny-11/PECH blends, $^{13}$C $T_1$ values were measured by the p.s.t./m.a.s. inversion-recovery pulse sequence shown in *Figure 4d*. Because $^{13}$C magnetization was built up by the p.s.t. method, signals of the crosslinked region of PECH and the crystalline Ny-11 phase might be missed. Mainly the resonances in mobile phases were detected. The low natural abundance of $^{13}$C nuclei eliminates the spin-diffusion process, and thus each carbon resonance shows its own relaxation time. Two $T_1$ components were observed for neat Ny-11. The longer $T_1$ component corresponds to the crystalline phase, the shorter one to the amorphous phase. Because the c.p. ability of each carbon resonance is different, and even the same carbon resonance shows differences in c.p. ability and $^1$H and $^{13}$C $T_{1\rho}$ in different phases (e.g. crystalline and amorphous phases), the observed composition of the longer $T_1$ component does not simply correlate to the crystallinity. Note that the $T_1$ values of all carbon resonances of PECH increase as Ny-11 component increases, while the values of Ny-11 component in the blends (mainly amorphous phase here) are almost the same as those of the shorter $T_1$ values of neat Ny-11. These results indicate that the phase structure of PECH component is changed after blending with Ny-11. But the change is unpronounced for the amorphous phase of Ny-11.

The long $^{13}$C $T_1$ value of the crystalline phase of Ny-11 makes it possible to select the spectrum of this crystalline

**Table 3** The $^{13}$C chemical shift (ppm) and linewidth (Hz) of Ny-11/PECH blends at 25°C[a]

| | Ny-11 | PECH | | |
|---|---|---|---|---|
| Resonances | C=O | CHO | $CH_2O$ | $CH_2Cl$ |
| Ny-11 | 173.2<br>(160) | | | |
| Ny-11/PECH = 75/25 | 173.5<br>(170) | 79.0 | 69.8 | 44.1 |
| Ny-11/PECH = 50/50 | 173.8<br>(180) | 79.1<br>(440) | 69.9<br>(480) | 44.1<br>(370) |
| Ny-11/PECH = 25/75 | 173.5<br>(200) | 79.6<br>(410) | 69.7<br>(470) | 44.0<br>(330) |
| PECH | | 79.3<br>(370) | 69.8<br>(460) | 44.1<br>(310) |

[a] The value of linewidth is shown in parentheses. Signals of PECH in Ny-11/PECH = 75/25 blend are weak and the linewidth is not given

**Table 4** $^{13}$C $T_1$ values (s) of Ny-11/PECH blends at 25°C

| | PECH | | | Ny-11 | | | |
|---|---|---|---|---|---|---|---|
| Resonance (ppm) | 79 | 70 | 44 | 40–43 | 36 | 32–34 | 31 |
| Ny-11[a] | | | | 0.45<br>(79%)<br>6.6<br>(21%) | 0.56<br>(82%)<br>10<br>(18%) | 0.80<br>(74%)<br>11<br>(26%) | 0.38<br>(90%)<br>13<br>(10%) |
| Ny-11/PECH = 50/50 | 0.91 | 0.54 | 0.30 | 0.46 | 0.55 | 0.79 | 0.35 |
| Ny-11/PECH = 25/75 | 0.83 | 0.50 | 0.28 | 0.49 | 0.53 | 0.82 | 0.36 |
| PECH | 0.66 | 0.37 | 0.23 | | | | |

[a] Two-component $^{13}$C $T_1$ was observed for neat Ny-11. The value in parentheses represents $^{13}$C number percentages of the two components

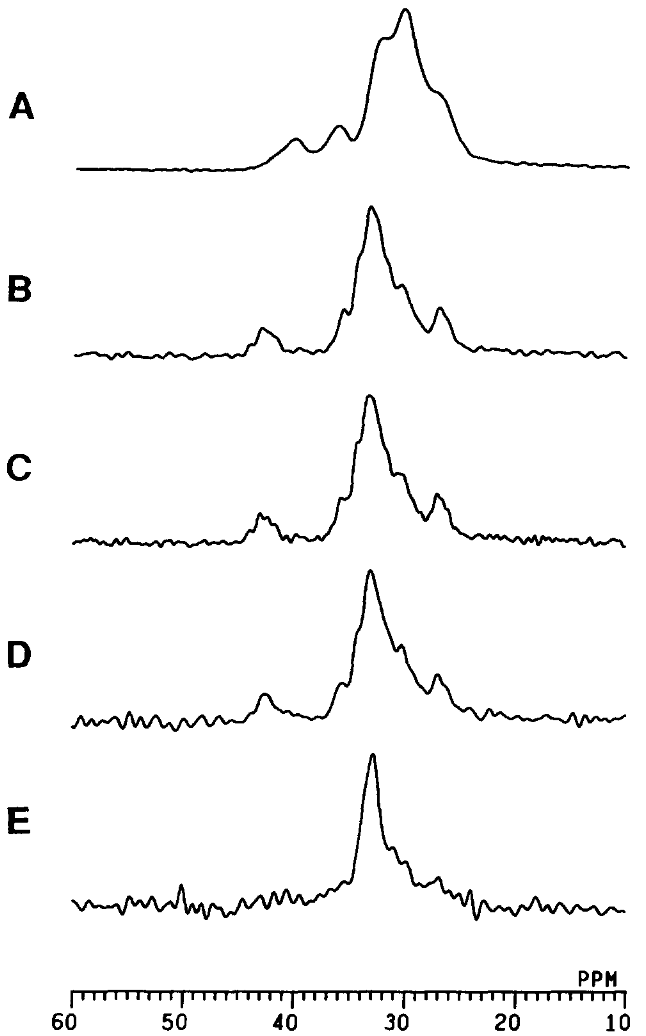

**Figure 5** (A) The high-resolution solid-state $^{13}C$ spectrum of neat Ny-11 (crystalline and amorphous phases). Selected $^{13}C$ spectra of the crystalline phase of Ny-11 component in the blends observed by the Torchia pulse sequence with 3 s delay time at 25°C: (B) in neat Ny-11; (C) in Ny-11/PECH = 75/25; (D) in Ny-11/PECH = 50/50; (E) in Ny-11/PECH = 25/75

phase by the Torchia pulse sequence (*Figure 4c*). After a delay time of 3 s, which is 3–10 times longer than $T_1$ of both PECH and the amorphous Ny-11, only the resonances in the crystalline phase of Ny-11 remain. The observed spectra together with the normal c.p./m.a.s. spectra of Ny-11 (both crystalline and amorphous phases) are shown in *Figure 5*. The linewidth of the crystalline Ny-11 is narrower than that in the normal c.p./m.a.s. spectrum. Some peaks corresponding to the crystalline phase are noticeable after signals of the amorphous phase relax out. The $CH_2$ carbon bonded to the NH now appears at 42.9 ppm, and the $CH_2$ carbon bonded to the C=O appears at 35.6 ppm. The $CH_2$ peak at 27.0 ppm in the crystalline phase also becomes pronounced. Note that the spectra of Ny-11 crystalline phase in Ny-11/PECH = 75/25 and 50/50 blends are similar to that of neat Ny-11. We also observed resonances at 35–25 ppm of Ny-11 component in the 25/75 blend, for which no melting behaviour of the crystalline phase was observed in the d.s.c. study. Note that the $^{13}C$ $T_1$ value of the resonances at 32–34 ppm in amorphous Ny-11 is the same as that of PECH at 79 ppm (*Table 4*). After a delay time of 3 s, which is 3 times their $T_1$ values, both signals at 32–34 and 79 ppm should decrease to 5% of the original intensity. In this case, we still observed Ny-11 signals, but the resonance for PECH at 79 ppm is too weak to be noticed. This suggests that the Ny-11 component still contains a longer $^{13}C$ $T_1$ component in the 25/75 blend. Meanwhile, the linewidth of the Ny-11 component with a longer $^{13}C$ $T_1$ value in 25/75 blend is broader than those in the other blends and neat Ny-11. This component should correspond to the Ny-11 chains in a relatively rigid local ordered structure. The whole Ny-11 component in 25/75 blend may not be completely amorphous although no melting behaviour of the Ny-11 crystalline phase can be detected at the sensitivity of d.s.c.

Usually the decrease of the crystallinity and changes of phase structures of crystalline polymers occur in intimately miscible blends[25–28]. For immiscible blends, the crystallinity usually decreases less, but the domain structure and domain size may be changed by the blending, as found in, for example, polyamide-6/ethylene–vinyl alcohol copolymer (Ny-6/E-VOH) blends[5] and poly(phenylene sulfide)/poly(ether sulfone) blends[28]. For Ny-6/E-VOH blends, the $^{13}C$ $T_1$ of the amorphous Ny-6 shows no change but that of the crystalline phase changes significantly after blending, corresponding to the decrease of crystalline domains of Ny-6 in the blends[5]. The same thing probably happens for Ny-11/PECH blends. Although the domain size of the blends is large (1–2 μm), the crystalline perfection of the Ny-11 crystal could be worse and the crystalline size could be smaller after blending Ny-11 with PECH. When PECH is rich, the crystalline phase of Ny-11 is destroyed to a large extent, and only some local ordered structures of Ny-11 chains exist in the blend.

For more information about the motional states of Ny-11/PECH blends, $^1H$ spin–spin ($T_2$) and spin–lattice ($T_1$) relaxation times were measured as shown in *Table 5*. $^1H$ $T_1$ relaxation times of both neat PECH and Ny-11 at 50°C are single values, probably because the $T_1$ value of each component in the two neat polymers happens to be too similar to be distinguished, respectively. Strong spin-diffusion coupling within the two neat polymers also plays a certain role for the single $T_1$ relaxation time. But the $T_1$ values of the two polymers are different enough to be used for examining phase structures of the blends. Because the domain size of the blends is rather larger (1–2 μm) than the characteristic maximum spin-diffusion path length during $T_1$ times (about 100 Å), we can assume that the spin-diffusion coupling interaction between the two polymers is weak. Thus, the longer $T_1$ component of the blends should correspond to the Ny-11 component, and the shorter one to the PECH component. After blending, the $T_1$ values of both components become shorter as the second component increases in the blends. These results also reflect the changes of motional states/phase structures of the two polymers in the blends.

The $^1H$ $T_2$ decay of PECH shows three components at 30°C. The fast Gaussian decay with a short $T_2$ value ($T_{2S}$) corresponds to the crosslinked region. The longer $T_2$ component ($T_{2L}$, Lorentzian decay) is due to the free region of PECH, while the $T_{2I}$ (Lorentzian decay) is due to the intermediate region. Mainly a single Gaussian decay was observed for semicrystalline Ny-11 at 30°C. The longer $T_2$ component (3%) may correspond to a small amount of impurities. All blends show three $T_2$ components. Note that the $T_{2L}$ values of 75/25 and 50/50 blends become shorter compared to that in pure PECH. These indicate that the mobility of the free region of

**Table 5** $^1$H $T_2$ values (μs) at 30 and 60°C, and $T_1$ values (ms) at 50°C of Ny-11/PECH blends[a]

| Samples | Ny-11 | 75/25 (86/14) | 50/50 (68/32) | 25/75 (41/59) | PECH |
|---|---|---|---|---|---|
| $T_2$ 30°C $T_{2S}$ | 8(97%) | 7(75%) | 7(50%) | 9(30%) | 10(8%) |
| $T_{2I}$ | | 82(7%) | 74(25%) | 84(38%) | 83(50%) |
| $T_{2L}$ | 121(3%) | 182(18%) | 268(25%) | 403(32%) | 291(42%) |
| $T_2$ 60°C $T_{2S}$ | 10 | 9(75%) | 9(51%) | 10(31%) | 10(5%) |
| $T_{2L}$ | | 640(25%) | 660(49%) | 780(69%) | 830(95%) |
| | | 25(14%) | 27(34%) | 26(56%) | 36 |
| $T_1$ | 110 | 118(86%) | 105(66%) | 85(44%) | |

[a] The values in parentheses show percentages of the components in proton number

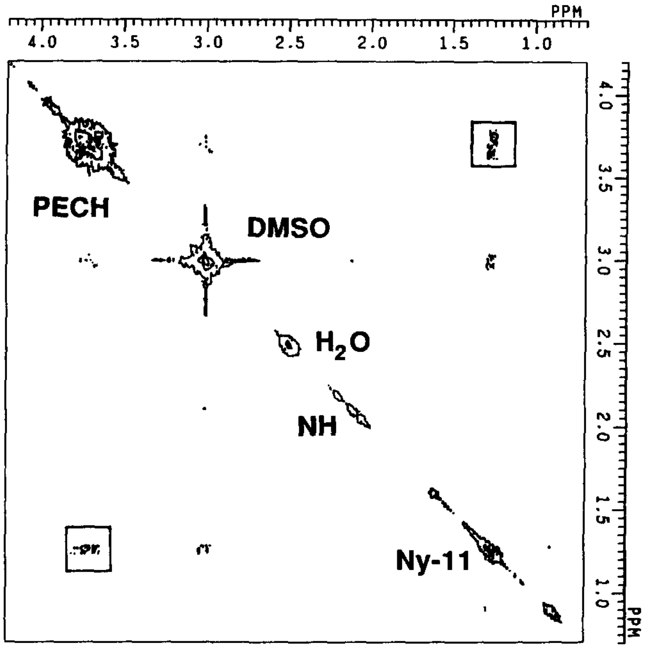

**Figure 6** The 2D-NOE spectrum of Ny-11/PECH system in DMSO solution at 100°C observed at a mixing time of 300 ms. Intermolecular negative NOE cross-peaks are enclosed by boxes

PECH component decreases to a certain extent in Ny-11-rich blends. Surprisingly, the $T_{2L}$ value of 25/75 blend is longer than that of pure PECH. At 60°C, Ny-11 shows a single $T_2$ decay. The small amount of the longer $T_2$ in Ny-11 is difficult to detect because of its rather longer $T_2$ value and small intensity. PECH, as well as all blends, appears as two $T_2$ components at 60°C. The $T_{2S}$ values of all blends are quite similar to those of pure Ny-11 and the crosslinked PECH. But the $T_{2L}$ value of the blends, mainly due to the PECH component, decreases as the Ny-11 composition increases at 60°C, even for 25/75 blend. Considering the results of both $^{13}$C and $^1$H $T_1$ studies, which indicate a change of phase structures of PECH component, the $^1$H $T_2$ result further indicates that free chain motions above $T_g$ of PECH chains are restricted to some extent after blending with Ny-11, although the effect on $T_g$ value of PECH component is not pronounced (the $T_g$ values of PECH component do not increase as Ny-11 increases in the blends). This phenomenon is quite similar to the crosslinking effect on molecular motions of PECH[24].

Note that the proton numbers of the ($T_{2I}+T_{2L}$) at 30°C and the $T_{2L}$ at 60°C are all more than 10% higher than the proton number of PECH introduced into the blends (see *Table 5*). This suggests that some protons of the Ny-11 component also contribute to the longer $T_2$ components. Besides impurities and trace amount of water in Ny-11, which are about 3% as seen at 30°C, it is also possible that a small amount of Ny-11 chains located near PECH phase are induced by mobile PECH chains; thus they have a similar mobility as PECH phase. Certainly, these Ny-11 chains should show a significant difference in $^{13}$C relaxation behaviour. However, their amount is too small, and thus these mobile chains were missed in the $^{13}$C $T_1$ measurement, although the p.s.t. method is sensitive to mobile phases.

In the $^1$H high-resolution spectrum of Ny-11/PECH system in DMSO solution, resonances of linear PECH are all located in the field range of 3.6–3.8 ppm, while $CH_2$ proton resonances of Ny-11 are at 0.8–1.7 ppm, mainly 1.2–1.3 ppm. The resonances of the two polymers are well separated without any overlapping. This makes it possible to carry out a NOE study. In 2D-NOE spectra, the intense diagonal peaks contain the same information as a normal 1D spectrum, and the cross-peaks show the resonance frequency of those protons that contact close enough to give rise to a strong dipole–dipole interaction. Since the strength of the dipole–dipole interaction is related to the sixth power of the inverse of the inter-proton distance, an inter-proton distance greater than 4 Å would be too large to cause appreciable NOE[29]. 2D-NOE spectra of Ny-11/PECH system at polymer concentration of 10% in DMSO solution were observed at a mixing time in the range of 10–500 ms at 100°C. When the mixing time is longer than 100 ms, positive NOE cross-peaks (negative NOE) between protons of Ny-11 and PECH were observed. A 2D-NOE spectrum at a mixing time of 300 ms is shown in *Figure 6*. The NOE cross-peaks between protons of Ny-11 and PECH are shown in boxes of *Figure 6*. The result indicates that the inter-proton distance between the two polymers is less than 4 Å in DMSO solution at 100°C. Since Ny-11 contains both NH and C=O groups while there are oxygen and chlorine atoms in PECH, possible interactions between the two linear polymers may be intermolecular hydrogen-bonding interactions and dipolar interactions, which cause the system to be miscible in the solution state. Unfortunately, the NH proton resonance is broad and its intensity is very low; thus the intensity of NOE cross-peaks between NH protons of Ny-11 and

PECH protons are too weak to be observed. This makes it impossible to study these interactions in further detail as that in ref. 13.

Since intramolecular interactions within Ny-11 chains are very strong, blending conditions also play a key role in the miscibility of the blends. Mixing systems with hydrogen-bonding and dipolar interactions as dominant intermolecular interactions usually show lower critical solution temperature (*LCST*) behaviour. The interactions should be enhanced at lower temperatures. We can observe intermolecular NOE cross-peaks between Ny-11 and PECH at 100°C on stirring the solution at the same temperature for several hours before measurement. But after standing the solution at room temperature for a few days and without stirring the solution at a higher temperature first, the NOE cross-peaks at both 25 and 100°C are rather weak. This is probably because the solubility of Ny-11 in DMSO is poor at lower temperatures. But further increasing the temperature above 100°C could result in the dissociation of intermolecular interactions, and therefore phase separation.

## CONCLUSION

The present study indicates that intermolecular interactions between Ny-11 and linear PECH result in the system being miscible in the solution state (DMSO). For the mechanical blends in the solid state, although the domain size of the systems is 1–2 $\mu$m, blending does change the phase structures of the two components. The $T_g$ of the mobile PECH component does not increase after blending, but the existence of Ny-11 matrix hinders further free motions of PECH component to some extent about its $T_g$. The amorphous Ny-11 phase changes less after blending, but blending decreases the crystallinity and modifies the crystalline structure of Ny-11. For Ny-11/PECH = 25/75 blend, the crystalline phase of Ny-11 component has been destroyed to a great extent, and only some local ordered structures remain in the blends. The intermolecular interactions between the two polymers play certain roles for the uniform distribution of domains. The slight crosslinking of PECH and the mechanical blending make the blends retain a certain domain size but change the phase structures with dependence of blending composition. These are beneficial to provide good physical properties.

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