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Miscibility of poly(epichlorohydrin)/poly(vinyl acetate) blends investigated with high-resolution solid-state ^{13}C NMR

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Abstract

The miscibility of poly(epichlorohydrin) (PECH)/poly(vinyl acetate) (PVAc) blends were investigated by differential scanning calorimeter and ^{13}C cross polarization (CP) combined with magic angle spinning (MAS) spectroscopy. All the blends displayed single but increasing glass transition temperature with increased PVAc concentration. This indicates that the blend system is miscible on the scale of 10–30 nm for the entire composition. To examine the miscibility of the system on the scale below 10 nm, high-resolution solid-state ^{13}C nuclear magnetic resonance experiment was carried out. The measurement of cross polarization rate between proton and ^{13}C carbon nuclei (T_{CH}) showed that intermolecular cross polarization was slightly enhanced with increase of PECH composition. Single effective ^{1}H spin–lattice relaxation (T_1) time was found for PECH/PVAc. This observation suggests that interdomain spin–spin communications among all the protons in PECH/PVAc blends were possible on the scale of 10–30 nm, which is in good agreement with the DSC results. In the ^{1}H rotating-frame spin–lattice relaxation ($T_{1\rho}$) experiment, however, the blends displayed two-component exponential relaxation behavior, implying that interdomain spin–spin communications among all the protons were not possible within the time of ^{1}H $T_{1\rho}$. Therefore, the domain size is estimated to be 3–30 nm in diameter.

Keywords: Solid-state NMR; Miscibility; Polymer blends

1. Introduction

There has been considerable interest in the study of polymer blends due to the importance in academic and technical aspects. Experimentally, various techniques can be explored to characterize polymer blends, such as thermal and mechanical analyses, microscopy, light scattering and spectroscopic methods [1,2]. Solid-state nuclear magnetic resonance spectroscopy has proven to be a powerful technique for determining the scale of miscibility and phase structure of polymer blends, and for detecting specific intermolecular interactions, which has been one of our research interests [3–17].

^{13}C cross polarization combined with magic angle sample spinning (CP/MAS) and its various extensions or modifications are powerful tools to study the miscibility and phase structure of polymer blends. The various CP/MAS techniques may be divided into two classes according to the length scale to which they are sensitive [18,19], namely (1) short range (below 0.3 nm) and (2) long range (1–50 nm).

The two common short range techniques are (1) direct detection of ^{13}C chemical line shift and (2) measurement of cross polarization time constant (T_{CH}), respectively. Chemical shift is sensitive to the local electron density. If the local electron density is affected, say by hydrogen bonding, then a change in ^{13}C chemical line shift will be observed [12–14,20]. The cross polarization time constant characterizes the rate of polarization transferred from ^{1}H to ^{13}C. Carbons that are not bonded to hydrogens and have no close neighbor hydrogens need long T_{CH} to have their intensities increase to maximum. If the polymer components are miscible on the molecular scale, then intermolecular cross polarization can reduce to T_{CH} of the non-protonated carbons [19–21].

The long range techniques utilize the phenomenon of spin diffusion. Proton spin diffusion is not a physical movement of protons, but is rather a transfer of spin energy by successive energy-conserving spin flip-flops between a highly magnetized region to a less magnetized region [21–26]. The spin diffusion process may be modeled as a Fickian diffusion. Interdomain spin diffusion in polymer blends may be detected directly by ^{1}H CRAMPS (combination of rotation and multiple pulse spectroscopy), ^{1}H WISE (wideline separation), and Goldman–Shen experiments or

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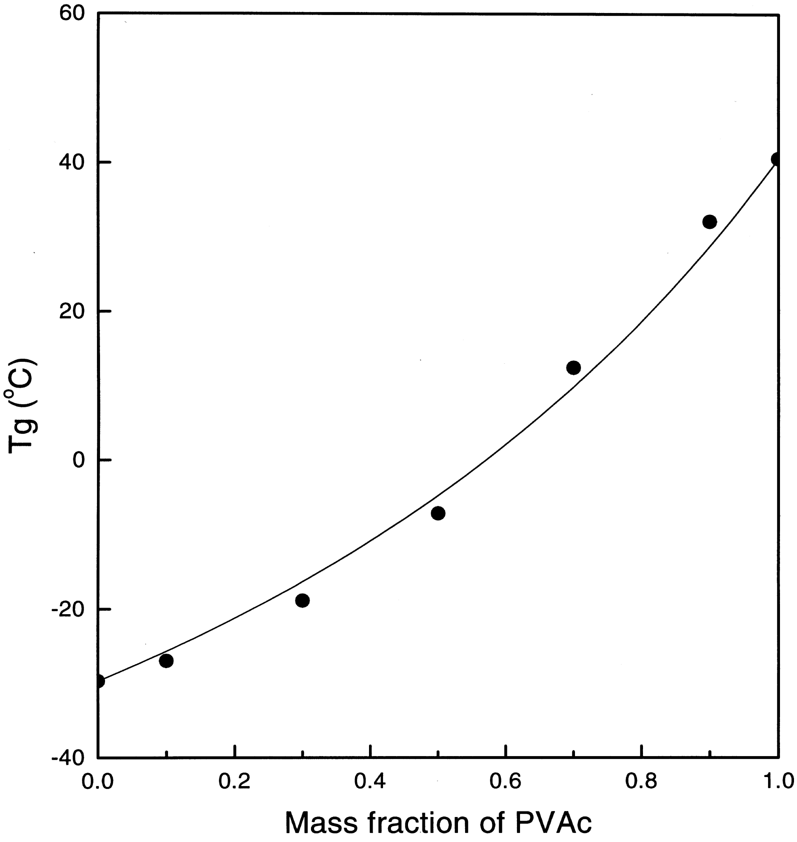

Fig. 1. Composition dependence of glass transition temperature of PECH/PVAc blends. The solid curve is predicted with the Gordon–Taylor equation using a *k* value of 0.55.

indirectly by its effects on proton relaxation times, ^{1}H T_1 and $T_{1\rho}$ [18,19,27–32].

^{1}H T_1 is measured at specific protonated carbon site by first having the protons gone through inversion-recovery before cross polarizing to ^{13}C. ^{1}H $T_{1\rho}$ is measured by monitoring the cross polarized ^{13}C intensity after a variable proton spin-lock time. The ^{13}C intensity is a function of the varying delay time, and it yields ^{1}H T_1 or $T_{1\rho}$ as the exponential time constant. When phase domains are on the order of 10 nm or less, interdomain spin diffusion averages out the ^{1}H T_1 of each different domain to one effective T_1 value. When the domains are greater than 50 nm, multiple T_1 and $T_{1\rho}$ are observed. During the period of ^{1}H $T_{1\rho}$ relaxation, proton spin diffusion covers a distance of about 3 nm. If one effective $T_{1\rho}$ is observed, it means that the domain size is below 1–3 nm. In this study, we adopted the CP/MAS scheme to investigate the miscibility of PECH/PVAc blends.

Previous differential scanning calorimetry (DSC) measurements of PECH/PVAc blends revealed a single glass transition temperature (T_g) that varied with blend composition [33]. It was concluded that PECH and PVAc are completely miscible at all compositions for temperatures below the cloud point curve. However, since DSC is suitable for probing a length scale of only 10–100 nm, it was premature to make such a conclusion. In order to investigate the miscibility of PECH/PVAc blends on the molecular length scale, ^{13}C CP/MAS techniques were used in the present work.

2. Experimental

2.1. Materials and preparation of blends

Poly(epichlorohydrin) (PECH) and poly(vinyl acetate) (PVAc) were both supplied by Scientific Polymer Products, Ont., NY, USA; PECH has a weight-average molecular weight $M_w = 700,000$ and PVAc has a weight-average molecular weight $M_w = 100,000$. All the PECH/PVAc blends were prepared by solution casting from cyclohexanone, the solvent was evaporated slowly at 60°C. The residual solvent was removed under vacuum at 60°C for four weeks.

2.2. Differential scanning calorimeter

The calorimetric measurements were made on a Perkin–Elmer Pyris 1 differential scanning calorimeter under a dry nitrogen atmosphere. The instrument was calibrated with indium and lead standard. The midpoint of the slope change of the heat capacity of the second heating scan was taken as

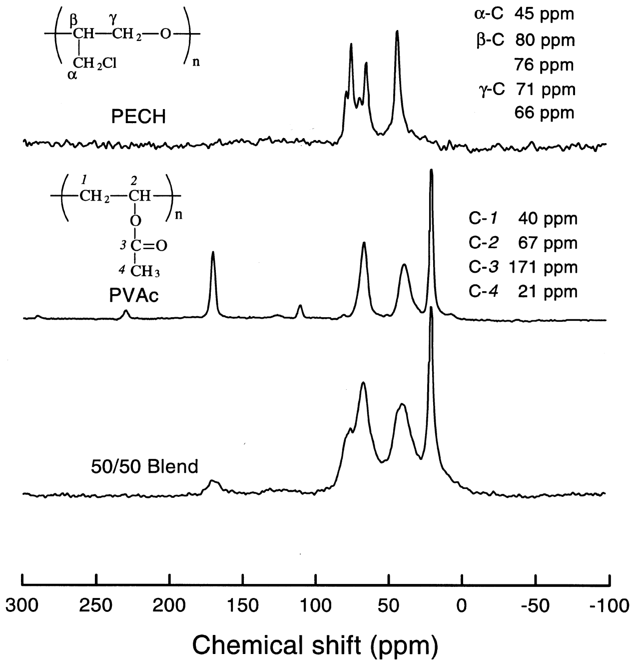

Fig. 2. ^{13}C CP/MAS spectra, and peak assignments for PECH, PVAc, and 50/50 blend.

the glass transition temperature (T_g). A heating rate of 20°C min^{-1} was adopted.

2.3. Solid state NMR

^{13}C CP/MAS spectra were measured at ambient temperature using a 9-T JEOL EX-400 NMR spectrometer. Samples were placed into 6 mm rotors. They were spun at the "magic-angle" (i.e. the angle between the sample spinning axis and the external static field being 54.7°). The ^{1}H 90° pulse width was 5.5 ms. Rotor spinning rates were between 5.5 and 5.9 kHz. The pre-delay time was 5 s. The number of accumulations for signal averaging is 1280. The external reference was Adamantane (ADM) which has two peaks at chemical shift values 29.5 and 38.6 ppm relative to tetramethylsilane (TMS).

^{1}H $T_{1\rho}$ and cross polarization transfer time constant (T_{CH}) were measured by varying the contact time. ^{13}C CP/MAS intensity increased initially until a maximum at contact time, $t_m = (T_{CH} \cdot T_{1\rho} \cdot /(T_{1\rho} - T_{CH})) \ln(T_{1\rho} \cdot /T_{CH})$. ^{1}H $T_{1\rho}$ was determined at larger contact times. T_{CH} may be calculated after t_m and $T_{1\rho}$ (H) were both measured [18]. The strength of the spin-lock field was 45 kHz. In ^{1}H T_1 measurements, ^{1}H magnetization first went through inversion-recovery before cross polarizing to ^{13}C for 1.0 ms. Subsequently, ^{1}H T_1 at specific carbon sites were measured.

Table 1
Cross polarization transfer time T_{CH} of carbonyl carbon in PECH/PVAc blends (the slight decrease in T_{CH} from 0.67 to 0.45 ms with increased wt% PECH suggests intermolecular cross polarization between carbonyl carbons of PVAc and hydrogens of PECH, but the interaction is not strong enough for miscibility on the molecular scale; glass transition temperatures T_g are listed alongside)

PECH/PVAc	T_{CH} (ms)	T_g (°C)
0/100	0.67	40.5
30/70	0.67	12.3
50/50	0.48	−7.2
70/30	0.45	−18.9
100/0	–	−29.7

3. Results and discussion

3.1. Differential scanning calorimetry

All the blends were subject to DSC measurement and the T_g data of PECH/PVAc blends are summarized in Fig. 1 as a function of composition. In accordance with previous result [33], the blends were miscible over the entire composition range as shown by the presence of the single glass transition temperatures that were intermediate between those of the pure components and regularly varied with the blend composition. Dependence of T_g's on the composition of the miscible polymer blends can be correlated with several empirical equations. One of such equations, Gordon–Taylor equation [34], has been extensively employed to predict the thermal behavior of miscible polymer blends:

$$T_g = ((W_1 T_{g1} + kW_2 T_{g2})/(W_1 + kW_2)) \quad (1)$$

where T_g is the glass transition temperature of the blends; T_{g1} and T_{g2} are those of pure components, PECH and PVAc, respectively. k is an adjustable fitting parameter that semi-qualitatively describes the strength of intermolecular interactions. If $k = 1$, then T_g would be a simple linear weighted-average of T_{g1} and T_{g2}, indicative of good miscibility between the two components. W is the weight fraction. The curve in Fig. 1 was drawn using the Gordon–Taylor equation with a k value of 0.55.

Our k value of 0.55 is different from the previous value of 0.62 obtained by Guo [33]. This discrepancy can be explained by the fact that our PECH has a lower glass transition temperature than Guo's, and our PVAc has a higher glass transition temperature than Guo's. We have repeated our DSC measurements and are, therefore, confident in our results.

3.2. High-resolution solid state ^{13}C nuclear magnetic resonance spectroscopy

Fig. 2 shows the ^{13}C CP/MAS spectra of PECH, PVAc, and a 50/50 blend. Peak assignments are made in the insets based on the literature [35,36]. The methine β-C of PECH splits into two peaks at 80 and 76 ppm. The methylene γ-C also splits into two peaks that are at 71 and 66 ppm. In the solid state, rotation about the C–O–C bond is highly restricted, therefore peak splittings due to conformational differences are observed. The higher-field peaks of the

Table 2
^{1}H $T_{1\rho}$ ms monitored at different carbon sites in PECH, PVAc, and their blends [α-C resonance (45 ppm) overlapped with C-1 peak (40 ppm), and γ-C peak (66 ppm) overlapped with C-2 peak (67 ppm) in the blends]

Carbon site	0/100	30/70	50/50	70/30	100/0
γ-C (71 ppm)	–	*S/N* low	*S/N* low	*S/N* low	1.4 ± 0.1
β-C (80 ppm)	–	*S/N* low	*S/N* low	*S/N* low	1.0 ± 0.1
β-C (76 ppm)	–	*S/N* low	1.5 ± 0.1 (63%) 8.5 ± 0.8 (37%)	1.8 ± 0.1 (59%) 9.1 ± 0.4 (41%)	8.9 ± 0.4
α-C/C-1 (45/40 ppm)	11.2 ± 1.2	3.4 ± 0.2	1.3 ± 0.1 (84%) 6.3 ± 0.6 (16%)	1.4 ± 0.1 (59%) 9.0 ± 1.5 (41%)	3.3 ± 0.2 (36%) 8.4 ± 0.4 (64%)
γ-C/C-2 (66/67 ppm)	11.3 ± 1.3	3.4 ± 0.2	1.6 ± 0.1 (64%) 5.1 ± 0.7 (36%)	1.4 ± 0.2 (57%) 9.7 ± 0.8 (43%)	9.2 ± 0.3
C-3 (171 ppm)	11.3 ± 0.8	4.5 ± 0.2	2.6 ± 0.1	2.9 ± 0.1	–
C-4 (21 ppm)	11.9 ± 0.5	4.0 ± 0.1	2.2 ± 0.1	1.7 ± 0.1	–

doublets, 76 and 66 ppm, mean higher shielding of the ^{13}C nuclei and are probably due to γ-*gauche* effects [37] or intermolecular dipolar interactions [36–41]. The upfield shift of 4–5 ppm is a typical value observed in *gauche* shielding effects of the γ-substituents CH_3 and Cl [37]. The chloromethyl α-C resonance peak (45 ppm) does not split into a doublet, but the ^{1}H $T_{1\rho}$ measured at this peak has two components. The longer component belongs to chloromethyl groups that are restricted by strong dipolar interactions with other chloromethyl and C–O–C moities [40]. The longer component $T_{1\rho}$ has the same magnitude as the $T_{1\rho}$'s of the shielded β-C and γ-C nuclei; therefore, it can further substantiate the presence of inter- or intramolecular interactions within PECH. The short component belongs to mobile chloromethyl α-C groups that are not restricted by inter- and intramolecular interactions. Intermolecular dipolar interactions are likely to be stronger in atactic PECH than in isotactic PECH [41].

Table 1 lists T_{CH} of carbonyl C-3, and glass transition temperatures T_g. We find that T_{CH} of carbonyl C-3 decreases from 0.67 to 0.45 ms with increasing wt% PECH. This suggests that there may be intermolecular cross polarization between carbonyl C-3 of PVAc and hydrogens of PECH. However, the improvement in cross polarization transfer

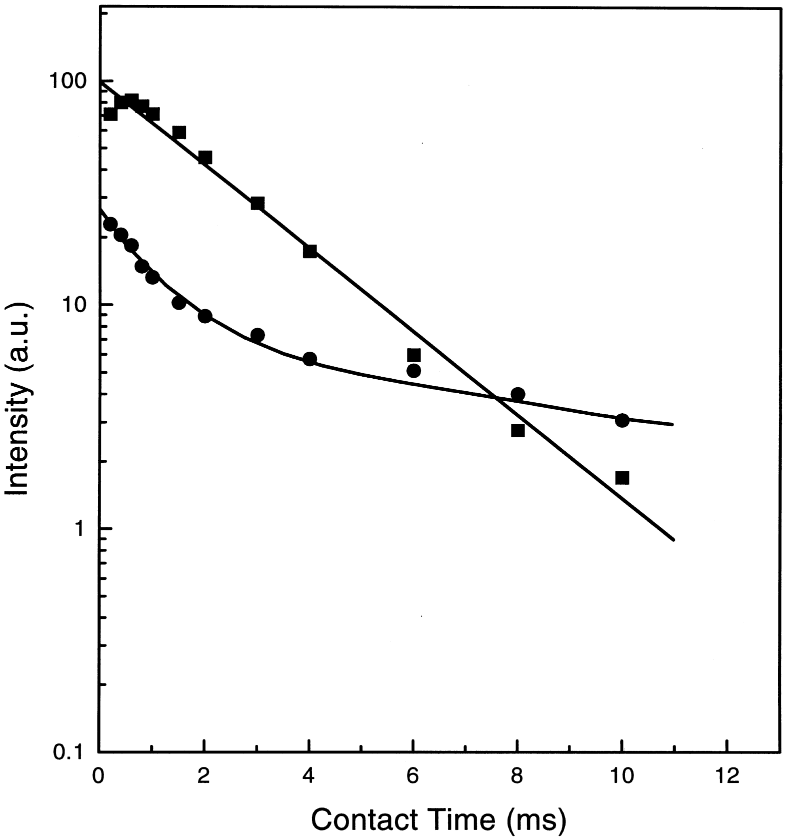

Fig. 3. ^{1}H $T_{1\rho}$ relaxation of PECH/PVAc 50/50 blend. Solid circles are for intensities taken at 76 ppm, and the solid squares for those at 21 ppm.

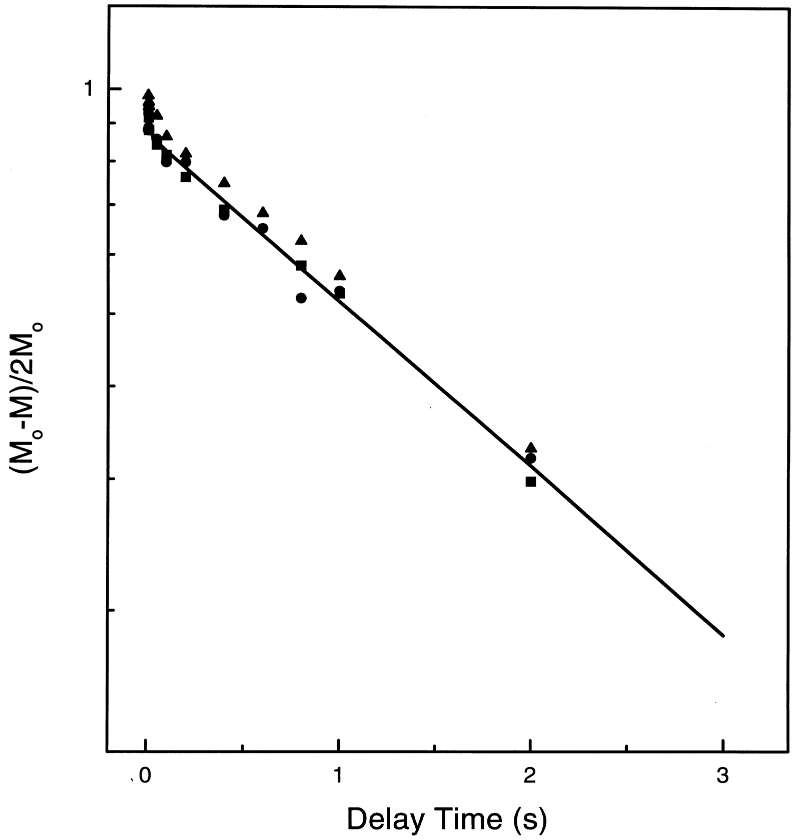

Fig. 4. ^{1}H T_1 relaxation of 50/50 blend is averaged to single exponential by spin diffusion phenomenon. The effective ^{1}H T_1 time is about 2 s.

efficiency is only marginal. Therefore, intermolecular hydrogen bonding, if any, between PVAc and PECH is not sufficient to affect mixing on the molecular scale. Furthermore, there is no observable downfield shift of C-3 peak, which is a signature of strong hydrogen bonding and intimate molecular mixing, with increased wt% PECH. The miscibility of PECH with PVAc was previously presumed to be due to hydrogen bonding between α-hydrogens of PECH and carbonyl C-3 of PVAc [33].

Table 2 lists the ^{1}H $T_{1\rho}$ of PECH, PVAc, and their blends monitored at different carbon sites. α-C resonance (45 ppm) overlapped with C-1 peak (40 ppm), and γ-C peak (66 ppm) overlapped with C-2 peak (67 ppm) in the blends. As listed in Table 2, ^{1}H $T_{1\rho}$ at an overlapping peak is measured. For blends that are above 30 wt% PECH, non-single $T_{1\rho}$ relaxations are observed at 76, 66/67, and 45/40 ppm peaks. Fig. 3 shows for a 50/50 blend that the $T_{1\rho}$ relaxation is single exponential at 21 ppm, but non-single exponential at 76 ppm. Spin diffusion did not average out ^{1}H $T_{1\rho}$ relaxations at all sites to a common value because the domain size is greater than 3 nm. Spin diffusion, however, averaged out all ^{1}H T_1 to a single value ~2 s (Fig. 4 and Table 3). Taking D to be at most 100 nm^2/s, a typical order of magnitude for rubbers, the upper domain size estimated from $d \leq \sqrt{6DT_1}$ is about 30 nm [31,42,43]. The size of the heterogeneities is, therefore, between 3 and 30 nm.

Table 3
^{1}H T_1 monitored at carbon sites in PECH/PVAc 50/50 blend (spin diffusion averaged out the T_1 to a single value ~2 s)

Chemical shift and peak assignment	^{1}H T_1 (s)
α-C/C-1 (45/40 ppm)	1.8 ± 0.1
β-C (76 ppm)	2.1 ± 0.1
γ-C/C-2 (66/67 ppm)	2.0 ± 0.1
C-3 (171 ppm)	2.0 ± 0.2
C-4 (21 ppm)	2.1 ± 0.2

4. Conclusions

The miscibility of poly(epichlorohydrin) (PECH)/poly(vinyl acetate) (PVAc) blends were investigated by differential scanning calorimeter (DSC). The blends exhibit single, composition-dependent glass transition temperatures that fit the Gordon–Taylor equation quite well with the adjusting parameter k of 0.55, suggesting a relatively weak intermolecular interactions. The heterogeneity of PECH/PVAc blend is on the scale of 10–30 nm in terms of single effective T_g characteristics measured with DSC. To examine the miscibility of the system at the molecular level, ^{13}C CP/MAS experiment was carried out. However, there is no observable downfield shift of the PVAc's carbonyl peak, which is a signature of strong hydrogen bonding with the PECH's α-hydrogen and an indication of molecular mixing. On the other hand, single values of ^{1}H T_1 were found for PECH/PVAc. This observation suggests that interdomain spin diffusion occurred fast enough among all the protons within the time of ^{1}H T_1. In ^{1}H $T_{1\rho}$ experiment, the blends displayed two-component exponential relaxation behavior, implying interdomain spin diffusion does not occur fast enough within the time of ^{1}H $T_{1\rho}$. Therefore, the domain size is estimated to be 3–30 nm in diameter.

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