

Interactions in Compatible Polymer Systems

1. Viscoelasticity and Glass Transition of Polystyrene-Poly(Vinylmethylether) Blends

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Summary

Dynamic mechanical measurements on polystyrene – poly(vinylmethylether) blends are demonstrating that the relaxation processes in the blends are mainly connected with the motions of the poly(vinylmethylether) chain.

Concerning the effect of mixing on topological properties of the blends, an increase of the polydispersity of the relaxation processes is detected in blends with high molecular weight polystyrene while low molecular weight polystyrene exerts an effect of dilution upon the relaxation of the high molecular poly(vinylmethylether) chains.

From these measurements as well as from thermoanalytical data it results that the energetic interaction is more pronounced in the blends with oligomeric than with high molecular weight polystyrene. The glass transition temperature shows a larger deviation from additivity for blends with high molecular polystyrene than for those with oligomeric polystyrene.

Introduction

Compatible polymer blends represent a challenge for systematical studies of the interrelations between the molecular parameters of the macromolecular components, their mutual interaction and their physical and applicational properties. Although two – and multiphase blends exhibit higher technological interest, basic information on compatible systems is the key for a final understanding of the more complicated systems. Benefit will be taken also from basic knowledge on compatible systems for studies concerning compatibilization of immiscible blends via strongly interacting groups.

Because compatible polymer blends are polymer – polymer solutions, it seems to be worthwhile to look for parallelsities with solutions of macromolecules in low molecular weight solvents and in oligomers.

Theoretical approaches, which take into account enthalpic demixing at low temperatures and entropy driven separation at higher temperatures are not too successful up to now in predicting critical phenomena ¹⁾. First attempts have been made ²⁾ to derive criteria for polymer blend compatibility from experimental data derived from polymer solutions in solvents, whose structure is analogous with that of segments of the second macromolecular component in the blend ^{3) 4) 5)}. The concept of group contributions to the thermodynamical behaviour, which is a base of the theoretical and the experimental approaches, is not distinctive enough, however, to make reliable predictions.

In a series of papers we will try to give contributions to the problems discussed. Compatible blends of polystyrene – poly(vinylmethylether) (PS – PVME) are attractive models for such studies. In this paper influences of interactions on the viscoelastic segmental motion in polystyrene – poly(vinylmethylether) blends will be treated.

Experimental

PVME (BASF) with $M_w = 73000$ has been chosen as the one component, PS with $M_w = 800$, $M_w/M_n = 1.3$ (PS₈₀₀) and $M_w = 75000$, $M_w/M_n = 1.06$ (PS_{75k}), respectively, as the other one. Thus an oligomer component offers the attractive chance to study viscoelastic effects of macromolecular and plasticizer action.

Mixtures with PS₈₀₀ have been prepared in melt under nitrogen atmosphere. Those with PS_{75k} were received by freeze-drying from toluene solution. Mechanical measurements were carried out with the INSTRON 3250 Rheometer in the cone-and-plate geometry, in the oscillating mode. With the system PVME-PS₈₀₀ they have been performed in the same temperature range for all compositions. The measured viscoelastic data range from the flow region through the rubber plateau up to onsetting of the glass transition region. With PS_{75k} as the second component only the mixture with 24.1 w. % PS could be investigated within the same temperature and modulus region.

T_g values have been determined with a PERKIN-ELMER DSC-2, the presented data being extrapolated for zero heating rate.

Results and Discussion

The Relaxation Time Spectrum

For all systems the storage and loss moduli and the dynamic viscosities have been determined. All master curves prove the validity of the time-temperature superposition principle. Thus the shape of the relaxation-time spectra is temperature invariant within the measured region, and the temperature influence on the viscoelastic behaviour occurs via the local flow process only, i. e. via the temperature dependence of the shift factors. In the following a strict discrimination between the mechanically initiated relaxation process and the local flow process appears to be therefore favourable.

In the terminal zone of viscoelastic behaviour a characteristic quantity for the width of the relaxation-time spectrum is given by the product of the stationary compliance, J_e^0 , and the storage modulus of the rubber plateau, G_N^0 ⁶):

$$G_N^0 J_e^0 = \left[\frac{\int_{-\infty}^{\infty} \theta^2 H(\theta) d \ln \theta / \int_{-\infty}^{\infty} \theta H(\theta) d \ln \theta}{\int_{-\infty}^{\infty} \theta H(\theta) d \ln \theta / \int_a^{\infty} H(\theta) d \ln \theta} \right]_{\theta=\theta(T_0)} = \left(\frac{\langle \theta \rangle_w}{\langle \theta \rangle_n} \right)_{T_0} \quad (1)$$

(a = Time of beginning of the rubber plateau)

G_N^0 and J_e^0 are defined as:

$$G_N^0 = \int_a^{\infty} \theta H(\theta) d \ln \theta \Big|_{\theta=\theta(T_0)} \quad (2)$$

$$J_e^0 = \frac{1}{\eta_0} \int_{-\infty}^{\infty} \theta^2 H(\theta) d \ln \theta \Big|_{\theta=\theta(T_0)} \quad (3)$$

J_e^0 is correlated with the zero shear viscosity, η_0 , and the characteristic constant, A_G , by:

$$J_e^0 = A_G / \eta_0^2 \quad (4)$$

These quantities are related via the relaxation time spectrum with the storage and the loss modulus ⁷⁾. Equ. (1) demonstrates that the product $G_N^0 J_e^0$ may be understood as the ratio of a two-moment order average and an one-moment order average of relaxation times. η_0 , A_G and G_N^0 can be estimated graphically. G_N^0 was identified with the inflexion point of the respective storage modulus master curve. Table 1 presents the results.

Table 1: Characteristic magnitudes of the relaxation time spectrum in the terminal zone. 1 - PS_{75k}, 2 - PVME. Blends of PVME with: 3 - PS_{75k}, 4 / 6 - PS₈₀₀ PS₈₀₀ could not be characterized in this way because of the missing rubber plateau

PS %w/w	T K	$\log \eta$ kPa.s ^{0.9} rad	$\log G_N^0$ kPa	$\log A_G$ kPa. (s/rad) ²	$\log J_e^0$ kPa ⁻¹	$\log (J_e^0 G_N^0)$	$\frac{\langle \theta \rangle_w}{\langle \theta \rangle_n}$	
1	100	439	0.92	2.11	-0.25	-2.09	0.02	1.05
2	0	310	1.11	2.23	1.26	-0.96	1.27	18.8
3	24.1	334	1.7	2.12	4.13	0.73	2.85	707
4	8.6	308	1.68	2.16	2.34	-1.02	1.14	13.8
5	24.2	308	1.45	1.9	2.11	-0.68	1.11	12.8
6	75.4	297	1.51	1.13	2.1	-0.92	0.21	1.26

Figure 1 illustrates the dramatic difference between mixtures with low and with high molecular weight PS. Oligomer PS acts like a solvent with respect to the relaxation time spectrum, whereas the high molecular PS broadens strongly the relaxation time spectrum in the flow region. Figure 2 visualizes clearly the increase of the polydispersity of the relaxation process for the 24.1 % / 75.9% mixture of PS_{75k} and PVME, where the isotherm G' -master curves are supplementary shifted to superpose at the inflexion points, G_N^0 .

Heterogeneous topological situation of chain segments in the PVME - PS_{75k} mixtures may cause this broadening of the relaxation time spectrum, due to the coexistence of interacting PVME-PS segments with non-contacting chains of identical structure, as demonstrated by FT-IR studies ⁸⁾.

Mixtures of PS₈₀₀ with PVME may be able, however, to contact quite quantitatively because of the short chain length of the former, exhibiting consequently a polydispersity of the relaxation process situated between those of the components. Onogi et al. ^{9) 10)} have demonstrated that this is also valid for mixtures of structurally identical polymers with different molecular heterogeneity, molecular weights exceeding entanglement length.

In the relaxation processes the PVME chains essentially are engaged as indicated by the fact that the apparent activation energy of flow of the mixtures is very close to that of pure PVME (see Figure 8). Both, the broadening of the relaxation time spectrum for the 24.1% - 75.9% PS_{75k} - PVME mixture and the relatively small activation energy of flow cause a small temperature coefficient of the viscoelastic properties, i.e. a relative flat isochrone master curve ¹¹⁾, as shown in Figure 3. It may be rememb-

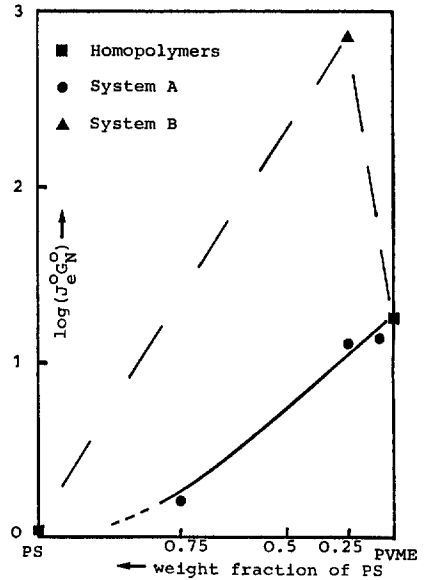


Figure 1: Plot of $\log (J_e^0 G_N^0)$ versus $\log (w.\text{fract. PS})$

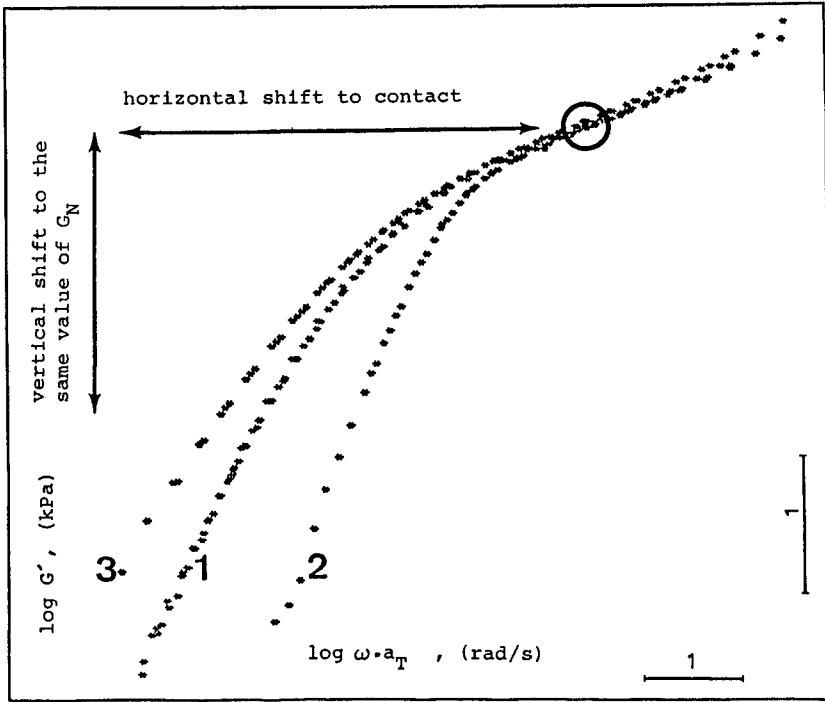


Figure 2: Comparison of the polydispersity of the relaxation processes in the terminal zone
 1. PVME_{73k} - 2. PS_{75k} - 3. mixture with 24.1% PS

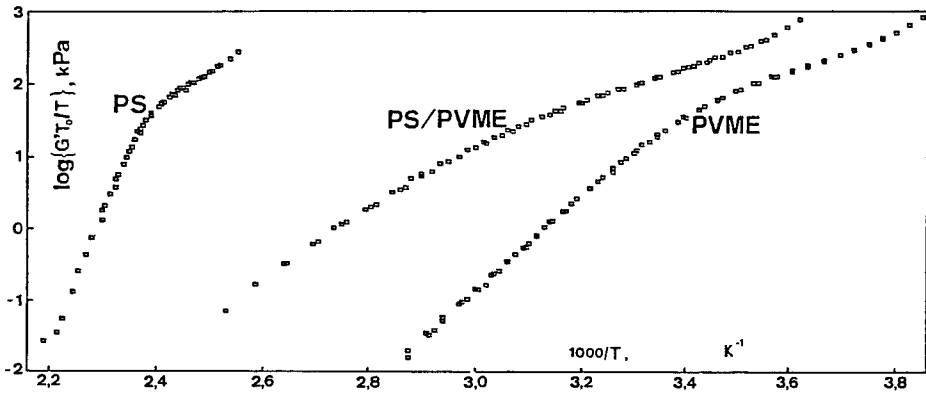


Figure 3: Isochrone master curves, $T_{red} = T_g + 120 \text{ K}$, $\omega_{ref} = 1 \text{ rad/s}$
 Samples as in Figure 2

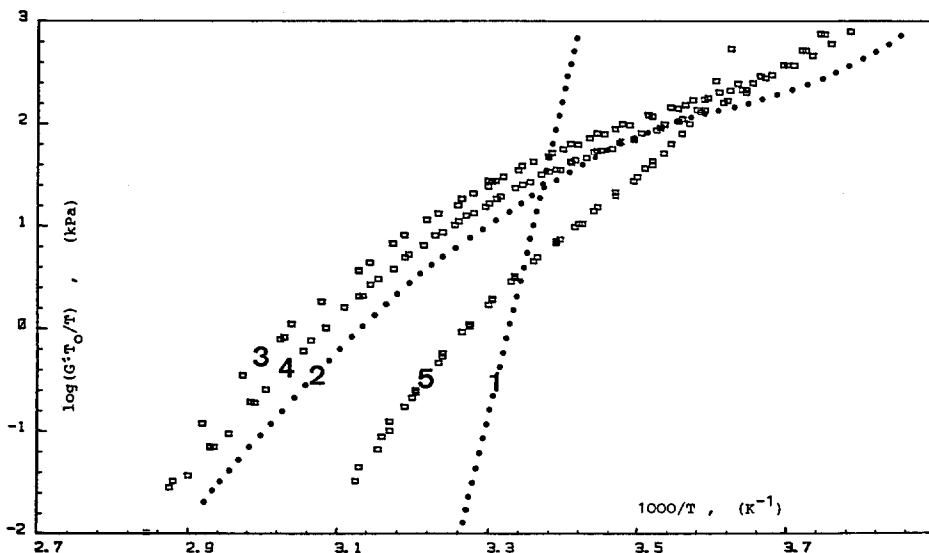


Figure 4: Isochrone master curves of G' of the mixture with oligomer PS. $T_{red} = T_g + 120$ K
 1. PS₈₀₀ - 2. PVME - 3. mixt. w. 8.6% - 4. mixt. w. 24.2% - 5. mixt. w. 75.4% PS₈₀₀

ered that the slope of the isochrone master curves is given by the product of the relaxation time spectrum and the activation energy [2]. The flat isochrone master curve suggests a tendency of the properties of the mixture to remove, with increasing temperature, from those of PVME, approaching those of PS.

The isochrone master curves with the oligomer PS₈₀₀ (Figure 4) exhibit different behaviour. For instance all mixtures with less than 50% PS₈₀₀ exceed the niveau of the storage modulus of both the components down to low temperatures. This again may be an indication of intensive PVME-PS contacts.

With respect to the changes of the relaxation time spectra, the mixtures with oligomer PS show parallelities to polymer solutions. An exponential dependence of the plateau modulus on polymer volume fraction, ϕ , is found for the PS₈₀₀-PVME, as reported for poly(butadiene) solutions [6]. $G_N^0 = 1.18 \cdot 10^2 \phi^{-2.22}$ has been reported for semi-diluted poly(butadiene) solutions and $G_N^0 = 1.66 \cdot 10^2 \phi^{-1.93}$ has been found for the PS₈₀₀-PVME blend (Figure 5).

After having discussed the influence of molecular interactions on the relaxation time spectrum of the studied polymer blends, their role in the local flow processes may be treated now.

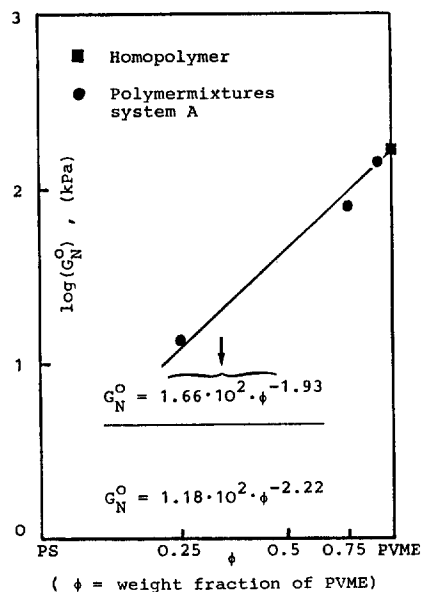


Figure 5: Influence of dilution of PS₈₀₀ on G_N of the mixtures

T_g and the Local Flow Process

Local flow processes are connected with the mobility of the polymer chains, and it is well known that the glass transition, T_g , is connected with that mobility. Consequently, T_g is used frequently as parameter when describing the temperature dependence of the local flow processes¹³⁾. As the chain mobility is influenced by both energetic and entropic interactions one may conclude that this is also reflected in the glass transition and in the local flow process.

The analysis of the T_g behaviour may be presented first. Figure 6 shows the T_g -data, including the available literature values of blends with high molecular weight PS.

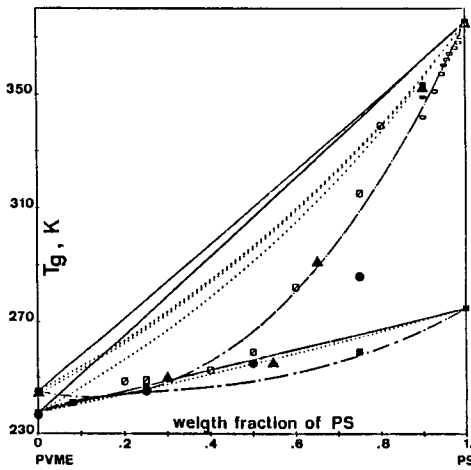


Figure 6: T_g -data of PVME / PS blends, literature data included. Own data:
 • PVME / PS_{75k} ■ PVME / PS_{800k}

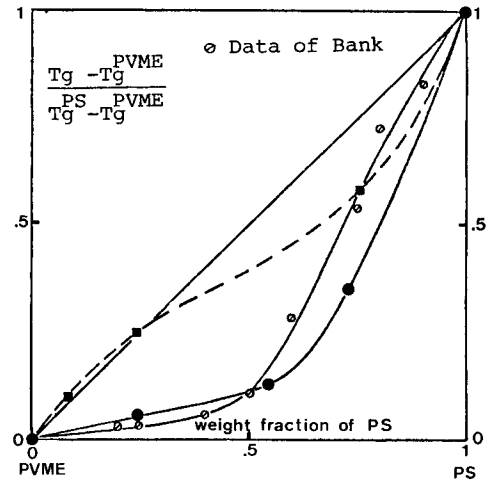


Figure 7: Reduced T_g -data of PVME / PS blends, sample data like in Figure 6

For both the blends of PVME, with oligomer and high molecular weight PS, the experimental data cannot be fitted by any of the empirical rules, which are supported by the thermodynamic mixing relations, assuming continuity of the extensive thermodynamic functions at T_g ^{15) 16)}. This is true for the common additivity rules, be they arithmetic or geometric mean rules (the latter the Fox relation¹⁷⁾), as well as for the Gordon-Taylor equation¹⁸⁾. Only the introduction of a supplementary adjustable term, as proposed by Kwei¹⁹⁾, enables the fit of the experimental T_g -data of the discussed blends.

For continuity of extensive thermodynamic functions at T_g , enthalpy and volume, respectively, the T_g of a polymeric binary compatible mixture is related with the T_{g_i} -values of the components accordingly to Couchman¹⁵⁾ by the expression

$$T_g = (K_1 w_1 T_{g_1} + K_2 w_2 T_{g_2}) / (K_1 w_1 + K_2 w_2) \quad (5)$$

where $K_i = \Delta C p_i$ in the enthalpic version and $K_i = V_i^0 \Delta \alpha_i$ in the volume version of the equation. The mole fraction X_i is replaced by the weight fraction, w_i . Introducing $K = K_2 / K_1$ and assuming $K = 1$ the arithmetic mean rule is obtained, whereas the acceptance of the Boyer rule²⁰⁾, $\Delta C p_i T_{g_i} \approx \text{const.}$, leads to the geometric mean relation of Fox.

Kwei introduces a supplementary correction factor, $q w_1 w_2$, for better fit of the experimental T_g -data of compatible blends:

$$T_g = (w_1 T_{g1} + K w_2 T_{g2}) / (w_1 + K w_2) + q w_1 w_2 \quad (6)$$

Figure 6 suggests, however, also a different behaviour of the PVME blends with oligomer and high molecular weight PS, respectively. According to the iso-free volume state assumption of the glass transition temperature, introduction of PS in PVME contributes generally to an increase of the fractional free volume, which manifests in lowering of the T_g of the blend. This increase in free volume is substantial for all compositions of the high molecular weight blend, whereas in the blend with oligomer PS the additivity rule is respected up to a PS content of about 40 - 50 w% PS. That means that the oligomer PS chain contacts more intensive with the mobile PVME chain than high molecular weight PS (Figure 6).

These effects are better evidenced if a normalized plot of T_g data is performed (Figure 7). For clarity only literature data of Bank et al. ¹⁴⁾ are included in the Figure.

From the dynamical mechanical data the apparent activation energy of flow has been derived. The dependence of this magnitude on composition of the PVME-PS mixtures and on reciprocal temperature is shown in Figure 8. The small increase of the apparent activation energy of flow by adding PS to PVME suggests that the mobility of the PVME chain is dominantly responsible for the local flow process up to high PS contents, i.e. the stiffer PS chains are floated by the moving PVME chains. The retarding effect of the PS on the flow of PVME increases with its molecular weight and by lowering the temperature. The molecular weight effect again suggests a better contact of the oligomer to the PVME than of the high molecular weight PS chain. Consequently the relative number of interacting sites will be higher in the blend with oligomer PS.

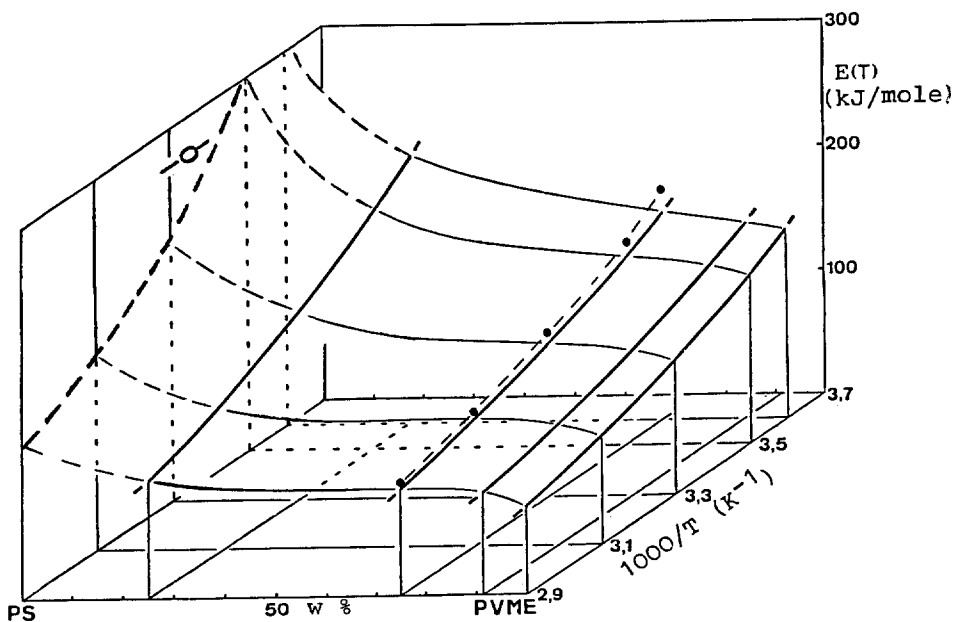


Figure 8: Plot of the $E(T)$ -values versus composition and reciprocal temperature for PVME and the PS-PVME-mixtures in the measured temperature range

- apparent activation energy for mixtures with PS₈₀₀
- apparent activation energy of flow for the mixture with 24.1 w% high MW PS
- extrapolated $E(T)$ -values for PS₈₀₀
- determined $E(T)$ -values for PS₈₀₀ from the very small analyzable T-range

It may be noted that mixtures with higher content of high molecular weight PS could not be measured in the same rheological geometry. Therefore these data are not included in the Figure.

Both T_g -data and rheological measurements suggest that the contact of the stiffer PS chain to the mobile PVME chain diminishes by increasing the molecular weight of the PS component. Consequently, the relative number of interaction sites between the chains decreases, contributing to an increase of the fractional free volume in the blend. Thus general decrease of the T_g of the blend will be effected. On the other hand the mobility of PVME will be more and more hindered by the increase of the volume of the contacting PS coil. A more detailed analysis will be presented elsewhere.

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