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Segmental Relaxation and the Correlation of Time and Temperature Dependencies in Poly(vinyl methyl ether)/Polystyrene Mixtures

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ABSTRACT: An analysis is presented of the glass transition dispersion in the dielectric spectrum of poly(vinyl methyl ether) (PVME) mixed with polystyrene (PS). The spectrum is dominated by the response of the PVME, enabling its molecular motions to be studied as a function of both local composition and temperature. It is shown that through their effect on the degree of intermolecular cooperativity of the segmental dynamics concentration fluctuations effect a marked asymmetry in the band shape. PVME chain units in a PS-rich environment contribute to the dielectric loss primarily at lower frequencies and are characterized by more cooperative segmental relaxation. The dielectric response of these segments is more sensitive to temperature than PVME segments relaxing in a PVME-rich environment. This results in a failure of time-temperature superpositioning. The correlation observed for the time and temperature dependencies of PVME relaxation near its glass transition temperature is a consequence of intersegmental cooperativity.

Introduction

Glass transition dispersions in the mechanical and dielectric spectra of miscible polymer blends are usually broader than the corresponding pure component relaxation spectra. The origin of this broadening is the distribution of segment environments engendered by concentration fluctuations.[1-4] These fluctuations displace the spectral dispersion over a distribution of frequencies corresponding to the distribution of effective relaxation times produced by the concentration fluctuations. Although in a miscible blend the latter are governed by the free energy of mixing and the details of its composition dependence, surprisingly the spectral broadening (at least for mixtures well removed from the two-phase region of the phase diagram) has been found to be unrelated to thermodynamic considerations.[5-7] Recently a model was proposed to account for the composition dependence and shape of segmental relaxation spectra of miscible blends near their glass transition temperature.[8] The concentration fluctuations are considered to affect the degree to which relaxation of a polymer segment involves neighboring chain units. By drawing on a coupling scheme for segmental relaxation in homopolymers,[9] it was shown that a connection exists between the apparent relaxation time of a mixture and the extent of intersegmental cooperativity of its molecular motions.[8] The coupling scheme predicts that more cooperative segmental relaxations exhibit larger time-temperature shift factors.[10,11] This was confirmed for poly(vinylethylene) and 1,4-polyisoprene, whose miscible blends exhibit such a correlation between their time and temperature dependencies.[8,11]

This report describes an analysis of the relaxation behavior of PVME in a blend with PS. The availability of dielectric relaxation measurements over a broad frequency range for this mixture near its glass transition[12] provided an opportunity to further assess this model of the chain dynamics in miscible polymer mixtures.

Application of the Coupling Model to Miscible Blends

According to the coupling model of relaxation[9] the fundamental intrachain conformational transition, as described by a Hall-Helfand type expression,[13] acquires a time dependence when interactions among neighboring segments build up to a degree sufficient to retard the relaxation. A detailed discussion of the model and its consistency with recent nuclear magnetic resonance measurements[14] is given elsewhere.[11] It has been shown[15] that at longer times when intermolecular coupling effects are manifested the relaxation of macroscopic variables proceeds according to the well known Kohlrausch-Williams-Watts function[16,17]

$$E(t) = E(0) \exp[-(t/\tau^*)^{1-n}] \qquad (1)$$

where τ^* is the apparent relaxation time and n the coupling parameter. This parameter is related to the degree of intermolecular cooperativity associated with the relaxation process, and thus provides a measure of the increase in the spectral breadth, or "effective distribution of material response times", over that of a linear exponential decay. The adherence to the Kohlrausch form of relaxation data for numerous polymers in the glass transition zone[1,8,10,11,18] is a consequence of the nature of their segmental relaxation. The effective relaxation time is related to the coupling parameter according to[9,19]

$$\tau^* = ([1-n]\omega_c^n \tau_0)^{1/(1-n)} \qquad (2)$$

In this expression τ_0 is one of the two primitive relaxation times in the Hall-Helfand function[13] and ω_c^{-1} is a characteristic time for the intermolecular couplings to begin to manifest themselves. For relaxations involving van der Waal interactions ω_c^{-1} is typically of the order 10^{-10} s.[9,19]

In a miscible blend the local environment will vary among segments due to concentration fluctuations.[1-4] Since the degree of cooperativity of the segmental relaxation is determined not only by the nature of the relaxing species, but also by this local environment, interchain interactions and correlations will fluctuate in accordance with the local compositional heterogeneity. This results in an inhomogeneous distribution of coupling parameters and effective relaxation times, which can be modeled with the assumption that the concentration fluctuations produce a normally distributed range of values for the coupling parameters of

Table I
Glass Transition Relaxation Results ($\phi_{\mathrm{PVME}} = 0.6$)

	eq 7				integral intensities[a]				
T, K	α	β	ϵ	τ_{HN}	τ_{cm}	$\tau_{+1/4}$	$\tau_{-1/4}$	$\tau_{+1/2}$	$\tau_{-1/2}$
275	0.25	1.01	3.0	3.5×10^{-3}	3.7×10^{-3}	6.1×10^{-4}	2.2×10^{-2}	7.6×10^{-5}	1.4×10^{-1}
281	0.28	1.01	3.1	3.5×10^{-4}	3.7×10^{-4}	7.0×10^{-5}	1.9×10^{-3}	1.0×10^{-5}	1.1×10^{-2}
291	0.38	0.92	3.8	2.2×10^{-5}	2.1×10^{-5}	6.1×10^{-6}	7.4×10^{-5}	1.4×10^{-6}	3.9×10^{-4}
297	0.42	0.98	4.1	7.0×10^{-6}	6.5×10^{-6}	2.1×10^{-6}	2.1×10^{-5}	5.4×10^{-7}	7.4×10^{-5}
305	0.46	1.01	4.4	1.5×10^{-6}	1.5×10^{-6}	5.4×10^{-7}	4.4×10^{-6}	1.6×10^{-7}	1.5×10^{-5}
311	0.48	1.03	4.5	6.0×10^{-7}	6.5×10^{-7}	2.4×10^{-7}	1.8×10^{-6}	7.6×10^{-8}	5.7×10^{-6}
316	0.49	1.22	4.4	2.0×10^{-7}	3.4×10^{-7}	1.4×10^{-7}	8.6×10^{-7}	4.8×10^{-8}	2.6×10^{-6}

[a] The respective inverse frequencies (in s) at which the integral intensity is down by 25% on the high (+1/4) and low (−1/4) frequency side, and down by 50% on the high (+1/2) and low (−1/2) frequency side of the band center. The band center is identified as the frequency, τ_{cm}^{-1}, at the center of mass of the dispersion.

each component. Assuming uniform strain the mechanical relaxation function for a blend is[8]

$$E(t)_{\mathrm{blend}} = \sum_i E_i(t) = \sum_i E_i(0) \int_0^1 \exp[-a_i(n_i - n)^2] \times \exp[-(t/\tau_i^*(\tau_{i0},n))^{1-n}]\,\mathrm{d}n \quad (3)$$

where the sum is over all chemical species comprising the blend (i.e., $i = 2$ for a two-component mixture), and $E_i(0)$ scales with the concentration of the ith component. Individual segments from all components contribute to the measured response with *an effective relaxation time*, τ_i^*, appropriate for their local environment as reflected in a particular n_i and τ_{i0}. These determine τ_i^* in accord with eq 2. Although the components are each associated with a different primitive relaxation time, the τ_{i0} for each is assumed to be uninfluenced by the compositional heterogeneities. Although integration limits from 0 to 1 are shown in eq 3, the actual limits correspond to the n appropriate for the extremes in local composition. From the relaxation modulus, $E(t)$, the mechanical loss modulus for the blend is obtained by[20]

$$E''(\omega) = \omega \int_0^\infty E(t) \cos(\omega t)\,\mathrm{d}t \quad (4)$$

According to eq 2 from the coupling model the spectral frequency of a dispersion is determined by τ_0 and n. Since τ^* depends nonlinearly on n, asymmetry in the broadening of the glass transition dispersion is expected for miscible blends. For example in blends of 1,4-polyisoprene and poly(vinylethylene), environments rich in the latter will confer to locally rearranging segments a large degree of intermolecular coupling, due to the higher T_g and larger n of pure poly(vinylethylene).[8,11] Both factors contribute to stronger intermolecular constraints and hence a larger n for these segments. It follows from eqs 2 and 3 that the contributions of such regions to the observed bulk relaxation will be to lower frequencies and will be broad relative to contributions at higher frequencies arising from polyisoprene rich environments. The extraordinarily low frequency tail observed in the mechanical spectra of these blends[6,8] is in accord with this prediction.

The heterogeneity of the segmental relaxation in polymer blends implies a breakdown of the principle of time–temperature equivalence,[7,8] although when measurements are carried out over a limited span of frequency or time, empirical time–temperature superpositioning is feasible. For example, master curves for mechanical spectra obtained at different temperatures in the transition region of blends of 1,4-polyisoprene and poly(vinylethylene) were constructed[8] notwithstanding the absence of thermorheological simplicity therein.

Shift factors are used to describe the temperature dependence of the effective relaxation time[20]

$$a_{i,n,T} \equiv \tau_i^*(n,T)/\tau_i^*(n,T_0) \quad (5)$$

where T_0 is an arbitrary reference temperature. Each component is associated with a distribution of n, and hence of shift factors. According to the coupling scheme these shift factors are related to the shift factors for the primitive relaxation time by[10]

$$(1 - n) \log a_{i,n,T} = \log a_{i,T}^0 \equiv \log [\tau_{i,0}(T)/\tau_{i,0}(T_0)] \quad (6)$$

This provides a test of the correctness of eq 3 in accounting for the relaxation behavior of miscible blends. The shift factors for broad relaxations, i.e., those characterized by stronger coupling (larger n), should exhibit a more marked dependence on temperature. Pure polymers have been found to exhibit this correlation between their time and temperature dependencies.[10,11]

Dielectric Spectroscopy Data

Experimental measurements obtained in the vicinity of the glass transition temperature on a blend containing a weight fraction, ϕ, of PVME equal to 0.6 have been reported.[12] The shape of the loss spectrum is particularly sensitive to the relaxation behavior. The empirical Havriliak–Negami function[21]

$$\epsilon'' = \frac{\Delta\epsilon \sin(\beta\psi)}{[1 + 2(\omega\tau_{\mathrm{HN}})^\alpha \sin(\tfrac{1}{2}\pi\alpha) + (\omega\tau_{\mathrm{HN}})^{2\alpha}]^{\beta/2}} \quad (7)$$

with

$$\psi = \arctan\left[\frac{(\omega\tau_{\mathrm{HN}})^\alpha \cos(\tfrac{1}{2}\pi\alpha)}{1 + (\omega\tau_{\mathrm{HN}})^\alpha \sin(\tfrac{1}{2}\pi\alpha)}\right] \quad (8)$$

was fitted to the dielectric loss modulus, ϵ'', versus circular frequency, ω, data for the blend by variation of the parameters α, β, $\Delta\epsilon$, and τ_{HN} using a nonlinear least-squares iterative procedure. The shape of the dielectric spectrum of the PVME/PS mixture is strongly temperature dependent, as seen from the variation in the Havriliak–Negami fitting parameters with temperature (Table I). No physical interpretation is associated with the obtained values for these parameters; the empirical Havriliak–Negami function is only used herein for extrapolation of the experimental measurements. The centers of mass of the spectra (the frequency at which the first moment equals 0) were determined for each temperature by numerical integration of the experimental data. By using eq 7 for the extrapolation, the extrapolated intensity was typically about 30% of the total integral. Other functions[22] could be employed to fit the dielectric measurements, but this would not significantly affect the results described below since errors in the fitting procedure are minified in the final analysis.

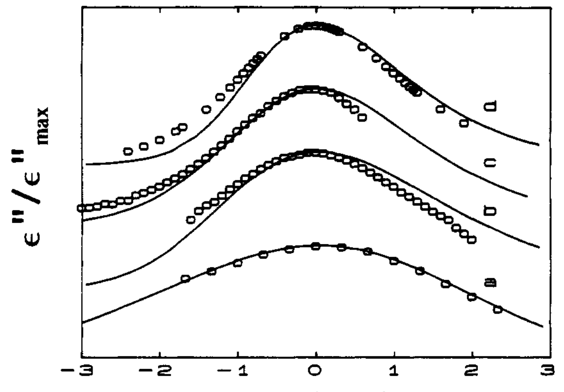

Figure 1. The dielectric response (+++) along with the best fit of eq 10 for the PVME/PS blend ($\phi_{\mathrm{PVME}} = 0.6$) at T = (a) 275 K, (b) 297 K, and (c) 316 K, and for (d) pure PVME at 292 K. The experimental data were taken from ref 12.

The frequency at which the integral intensity has decreased by a given amount identifies a particular local composition. The high-frequency side of the spectra corresponds to PVME-rich environments, while regions in which PS is more concentrated contribute intensity predominantly at lower frequencies. Since frequencies across the spectral bands correspond to various τ^* reflecting the local composition, a value of the coupling parameter can be associated with a given frequency through application of the blend model described above for mechanical spectra. The form of eq 3 appropriate for dielectric relaxation is (in the absence of local field effects)

$$\epsilon^*(\omega) - \epsilon_\infty = \sum_i \int_0^\infty \Delta\epsilon_i \int_0^1 -\frac{\mathrm{d}}{\mathrm{d}t}\left\{\exp[-a_i(n_i - n)^2] \times \exp\left[-\left[\frac{t}{\tau_i^*(\tau_{i0,n})}\right]^{1-n}\right]\right\}\exp[-i\omega t]\,\mathrm{d}t\,\mathrm{d}n \quad (9)$$

where ϵ_∞ is the limiting permittivity at high frequency and τ_i^* is calculated from eq 2. The actual integration limits in eq 9 assume values corresponding to a maximum (lower limit) and minimum (upper limit) local abundance of PVME. The dielectric loss is then

$$\epsilon'' = |\mathrm{Im}\ \epsilon^*(\omega)| \quad (10)$$

where any DC-conductivity contribution to the response[23] is neglected.

The experimental dielectric loss spectra for the blend were fitted to eqs 9 and 10. The factor $\Delta\epsilon_i$ depends on both the dipolar moment and concentration of the ith species. Since its dipole moment is much larger than that of PS,[12] PVME dominates the measured response and $\Delta\epsilon_{\mathrm{PS}}$ can be taken to be zero so that there is no summation over i in eq 9. This simplification leads to the dropping of all suffixes and dependencies on i in eqs 5 and 6, whereby all quantities now refer to PVME. The dielectric relaxation spectra can be interpreted solely in terms of the effect on PVME of its local environment.

Representative results of the fitting are shown in Figure 1. Since n is a function of the local composition, it varies across the spectrum. The imaginary term in the sum in eq 9 which has its maximum value at a given ω can be used to identify the coupling parameter associated with that frequency. Representative results for T = 297 K are listed in Table II. The mean value of the coupling parameter, n_{PVME}, for the blend (with $\phi_{\mathrm{PVME}} = 0.6$) is determined to be 0.67. The width at the half integral intensity points of the band encompass a range of n from 0.52 to 0.75 on the high- and low-frequency sides, respectively. This reflects the substantial distribution in the degree of intermolecular coupling of the relaxation of PVME segments due to the variation in local environment. The enhancement in the coupling of PVME segments in local environments richer in PS, in this blend whose total composition is fixed, is analogous to the increase in the average coupling parameter observed in PVE/PIP blends with increasing PVE content (see Figure 5 of ref 10).

Table II
Coupling Parameter Variation across the Blend Dispersion (T = 297 K)

	inverse frequency, s	n_{PVME}
$\tau_{-1/2}$	7.4×10^{-5}	0.75
$\tau_{-1/4}$	2.1×10^{-5}	0.71
τ_{cm}	6.5×10^{-6}	0.67
$\tau_{+1/4}$	2.1×10^{-6}	0.61
$\tau_{+1/2}$	5.4×10^{-7}	0.52

Time and Temperature Dependencies of Local Segmental Motion

Although the modeling displayed in Figure 1 is only semiquantitatively useful due to the absence of detailed knowledge concerning the specific effect of local composition on the degree of cooperativity of the relaxation dynamics, the assumptions underlying this approach can be tested. Unlike empirical representations of relaxation data (e.g., eq 7), the application of the coupling model to the inhomogeneous broadening in miscible blends offers verifiable predictions. Equation 2 describes the manner in which the apparent relaxation time, which determines the frequency at which a given local composition's contribution to the spectral dispersion is maximal, is related to both n and the local friction coefficient (via τ_0). The asymmetry seen in the PVME/PS blend spectra (Figure 1) is a consequence of this relationship. Moreover, eq 6 indicates that the interchain coupling of the segmental relaxation influences not only the shape of the relaxation function, but also its temperature dependence.[10,11] The temperature dependence of the relaxation times extracted from the dielectric data (Table I) are plotted in Arrhenius form in Figure 2. The conformance of these results to the VFTH function[20]

$$\omega^{-1} = \tau_\infty \exp\left[\frac{B}{T - T_\infty}\right] \quad (11)$$

can be seen. Data corresponding to the center of mass of the spectral dispersion can be associated with a concentration equivalent to the nominal blend composition ($\phi_{\mathrm{PVME}} = 0.6$). A glass transition temperature is defined by extrapolating the data for this central frequency (labeled as curve a in Figure 2) to that corresponding to an (arbitrary) time of 1 s. This yields T_g = 265 K for the blend. Note that this value should not be identified with the T_g determined, for example, by DSC.[24]

The temperature dependence of the data in Figure 2 for various local compositions are normalized using this T_g. The results are depicted in Figure 3 in the form of "fragility plots";[25,26] that is, the time–temperature shift factors are plotted versus T_g/T. The reference temperature for the shift factors is taken as T_g with τ(265 K) determined for each composition from the extrapolation of the VFTH equation (Figure 2). It is seen that the rank ordering of the "fragility" curves representing different local compo-

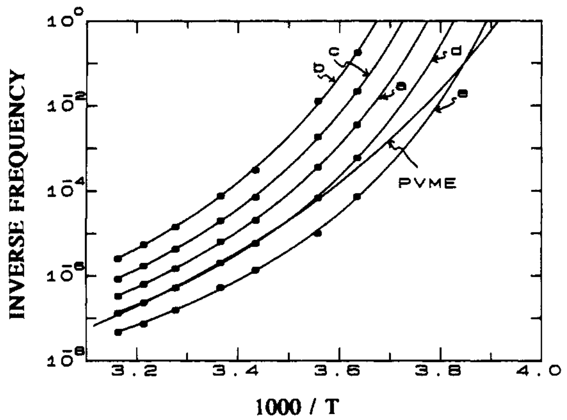

Figure 2. Arrhenius plots of the inverse of (a) the frequency of the center of mass of the glass transition dispersion for the PVME/PS blend, and the frequencies at which the integral intensity of the band is down by (b) 50% to lower frequency, (c) 25% to lower frequency, (d) 25% to higher frequency, and (e) 50% to higher frequency. The solid curves represent the results of fitting eq 12 to the experimental data, with $\tau_\infty = 1.35 \times 10^{-11}$ s, $B = 378.5$ K, and $T_\infty = 230.1$ K. The extrapolation of curve a to 1 s yields a glass transition temperature equal to 265 K for the blend. Also shown is data for neat PVME, the extrapolation of which yields $T = 257$ K at 1 s.

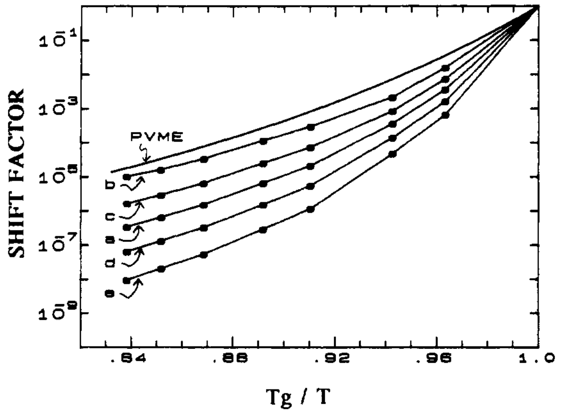

Figure 3. The inverse frequency, normalized by its value at the blend glass transition temperature ($T_g = 265$ K), as a function of the inverse temperature normalized by T_g^{-1}. The labels a–e for the curves are as defined in Figure 2. The coupling parameters associated with the various curves are tabulated in Table II.

sitions parallels the magnitude of the corresponding local coupling parameters. This agrees with previous results on pure polymers[10,11] and is consistent with the prediction of eq 6 that more intermolecularly coupled relaxations will exhibit more marked temperature dependencies.

Also shown in Figure 3 are data obtained from dielectric relaxation measurements on pure PVME.[12] A glass transition temperature for neat PVME is defined similarly as the temperature at which the central frequency corresponds to a relaxation time of 1 s. From fitting the loss spectrum at 292 K (Figure 1), a value of 0.56 was deduced for the n of neat PVME. It is seen that the results for the blend, extracted by modeling the inhomogeneously broadened spectra, are congruent with the pure PVME result. The local blend composition whose shift factors have a temperature dependence similar to that of pure PVME is characterized by a similar coupling parameter. Note also in Figure 3 that the curves for all compositions of blended PVME are steeper than that of pure PVME. This feature of the data is also consistent with the coupling scheme prediction (eq 6) when generalized to include pure PVME. These results demonstrate consistency in the analysis of the dielectric data by eq 9.

Discussion and Summary

In miscible blends of PVME and PS local compositional heterogeneity has been assumed to produce a distribution in the magnitude of the intermolecular constraints on segmental motion. A direct consequence of this dispersity is the asymmetry found in the spectral dispersion of the blend. The apparent activation energy of the shift factors is related to n; more intermolecularly cooperative segmental motions (larger n) exhibit shift factors more dependent on temperature. This correlation between time and temperature dependencies is reflected in the increased asymmetry in the loss spectrum as the temperature is reduced.

The response at higher frequencies arises primarily from regions in the mixture having higher concentrations of PVME. The coupling parameter deduced for segments in more PVME rich environments and the temperature dependence of their shift factors are found to approach those of pure PVME. This provides some validation of the premises of the analysis employed herein.

Implicit in the model is the failure of time–temperature superpositioning for miscible polymer blends. Such a breakdown was previously reported for the terminal region of the dynamic mechanical spectrum of blends of poly(ethylene oxide) with poly(methyl methacrylate).[27] A difference in entanglement densities of the blend components has been shown to contribute to differences in their terminal relaxation times and hence the absence of thermorheological simplicity.[28] Blend components are also associated with individual τ_{i0} (eq 9) reflecting their respective primitive friction coefficients. Together with the effect of local environment on intersegmental coupling, this produces the inhomogeneous line broadening and absence of thermorheological simplicity observed herein for the segmental relaxation of PVME blended with PS. The primitive relaxation time and the monomeric friction coefficient for the glass transition dispersion are identical to the corresponding quantities for the terminal relaxation. Differences in the components' primitive relaxation times thus will also give rise to differences in terminal relaxation times, with a consequent breakdown in time–temperature superpositioning in the terminal region.

A failure of time–temperature superpositioning was previously reported for PVME/PS mixtures;[29] however, that phenomena has a different origin than the present results. Even for pure polymers, shift factors obtained from the glass transition zone have a different temperature dependence than shift factors characterizing the terminal region of the spectrum.[30] This is a manifestation of the different viscoelastic mechanisms underlying the two dispersions.[31,32] The relaxation behavior of macromolecules at long times is governed by orientational rearrangements of the chain segments, while the shorter time response is dominated by more local distortional displacements.[33] The dielectric spectra analyzed herein are sensitive only to the glass transition dispersion, and unlike the earlier results for PVME/PS blends,[29] the absence of thermorheological simplicity is an explicit consequence of blending.

It should be emphasized that PVME/PS dielectric measurements are particularly useful for study the "fragility"[25] of the liquid state. Only the response of PVME is being measured, and hence the temperature dependence of specific molecular motions (e.g., backbone conformational transitions comprising the mechanism for segmental relaxation in PVME) can be investigated as a function of local environment.

In pure amorphous polymers, slight broadening toward higher frequencies of the glass transition dielectric dispersion is the norm.[34,35] A much greater broadening, with the asymmetry toward lower frequency, appears to be the usual situation for miscible blends. However, if the blend component contributing primarily at higher frequency (i.e., the lower T_g component) can provide a more constrained environment, broadening toward higher frequencies would be expected. Since both higher T_g and larger n strengthen intermolecular constraints, the particular composition necessary to realize this form of asymmetry is uncertain. A mixture whose components have slight differences in glass transition temperature but large differences in n would be an interesting subject for investigation. Currently we are applying the model to a number of other systems in order to assess its adequacy in describing blends with various combinations of glass transition temperatures and coupling parameters of the components.

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Registry No. PVME (homopolymer), 9003-09-2; PS (homopolymer), 9003-53-6.