

Surface Behavior of Dilute Blends of Poly(vinyl chloride) with Siloxane–Urethane–Ethyleneoxide Oligomers

M. M. GORELOVA,¹ A. J. PERTSIN,^{2,*} I. O. VOLKOV,² L. V. FILIMONOVA,² L. I. MAKAROVA,² and A. A. ZHDANOV²

¹Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, 70 Profsoyuznaya Str., Moscow 117393 and

²Institute of Organo-Element Compounds, Russian Academy of Sciences, 28 Vavilov Str., V-334, GSP-1, Moscow 117813, Russia

SYNOPSIS

X-ray photoelectron spectroscopy is used to study the surface segregation of siloxane in blends of poly(vinyl chloride) with siloxane–urethane–ethyleneoxide oligomers. At high concentrations of the oligomeric additive, the surface segregation of siloxane in the blends strongly depends on the molecular architecture of the additive: the segregation is much higher when the siloxane blocks are at the ends of the oligomeric chains. At low additive concentrations, the surface segregation of siloxane is governed solely by the siloxane concentration in the bulk. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Surface segregation of components of lower surface energy is a phenomenon inherent in all multicomponent systems. A distinguishing feature of multicomponent polymeric systems, such as copolymers or polymer blends, is that the extent of surface segregation strongly depends on the molecular architecture of the polymer, i.e. on the way in which the components are linked together by chemical bonds.^{1,2} Thus, for a given bulk composition and chain length, the surface segregation of a low surface energy component A will be different in an AB diblock copolymer, BAB triblock copolymer, B-*g*-A graft copolymer, and a blend of A and B homopolymers.

The effect of the polymer architecture on surface segregation can be rationalized in terms of constraints applied on the lower surface energy component by the other components of the system. In multiblock copolymers, for example, the surface segregation of the blocks of the lower surface energy component is constrained by the chemical links at both ends of the blocks. In diblock copolymers, there

is only one constraining link and more freedom to segregate, whereas the components of homopolymer blends are not linked at all and possess the greatest ability to segregate.²

Although the surface behavior of individual copolymers and blends of homopolymers has been understood fairly well,^{3–9} not much is known about polymer systems with a more complex architecture, such as blends of different copolymers or blends of copolymers with homopolymers. The most extensively studied system of this kind is a blend of AB block copolymer in B homopolymer, with the lower surface energy component being A.^{2,10} The surface–bulk compositional curves in such blends are generally “S”-shaped. With increasing concentration of the copolymer additive, the blend surface tends to attain a composition equivalent to that observed on the surface of the pure AB block copolymer. This suggests that the copolymer additive forms a continuous overlayer on the blend surface; the overlayer is sufficiently thick, so that the structure of its outer surface is not affected by the underlying homopolymer base. When the concentration of the copolymer additive is decreased, the thickness of the overlayer reduces and the additive macromolecules assume preferential orientation parallel to the sample surface. If the overlayer remains continuous, the observed surface composition tends to the stoichio-

* To whom correspondence should be addressed.

metric composition of the pure block copolymer additive.²

In our recent studies^{11,12} we have extended the surface studies of multicomponent polymers of complex architecture to three-component systems, namely, blends of a copolymer of A and B in a homopolymer of C. It was found, in particular, that multiblock copolymers of dimethyl siloxane (DMS) and bisphenol A carbonate (BAC), when added to poly(vinyl chloride) (PVC), can also form continuous overlayers with a surface composition typical of the surface of the neat block copolymers. On the other hand, blends of PVC with graft copolymers of methyl methacrylate (MMA) and DMS did not exhibit this trend. Moreover, in blends of some MMA-*g*-DMS copolymers with PVC, siloxane segregated to the surface to a much greater extent than it did in the pure MMA-*g*-DMS copolymers. In other words, it was as if the polymer base (PVC) promoted the surface segregation of the low energy component in the polymer additive (MMA-*g*-DMS copolymer).

A practical aspect of the cited work^{11,12} was to find the most efficient surface modifier of PVC with siloxane, i.e. a modifier that provides, when blended with PVC, a complete surface coverage with siloxane at the lowest concentration of the modifier in the bulk. The most efficient modifier was found to be one of MMA-*g*-DMS copolymers, which offered 100% surface siloxane at only 0.5% copolymer in the bulk.

In this work we investigated the surface behavior of one more type of multicomponent polymer system with a complex molecular architecture. More specifically, we studied the surface segregation of siloxane in blends of PVC with four siloxane-containing oligomeric additives of ABA and BAB triblock types. One objective of the work was to assess the efficiency of such additives as surface modifiers of PVC, in comparison with multiblock and graft copolymers studied before.^{11,12} Another objective was to analyze the dependence of surface segregation of siloxane in the blends on the position of the siloxane block in the oligomer chain (either in the middle or at the ends).

EXPERIMENTAL

The chemical structure of the oligomeric additives used can conveniently be represented as E-S-E and S-E-S, where E stands for an ethylene oxide (EO) block, $[\text{OCH}_2\text{CH}_2]_n$, S for a DMS block, $\text{Si}(\text{CH}_3)_2[\text{OSi}(\text{CH}_3)_2]_k$, and the dash for a diurethane (DU) joint, $\text{CH}_2\text{O}(\text{CH}_2)_2\text{OC}(\text{O})\text{NHC}_6\text{H}_5-$

$(\text{CH}_3)\text{NHC}(\text{O})\text{O}$. The chain of the E-S-E oligomers was terminated by hydroxyls; that of the S-E-S oligomers was by β -oxyethoxymethylene groups. The DMS blocks were of length $k = 21$ in all four additives; the EO blocks were of two different lengths, $n = 8$ and 34. The corresponding DMS-DU-EO oligomers will hereafter be designated as $\text{E}_8\text{-S-E}_8$, $\text{S-E}_8\text{-S}$, $\text{E}_{34}\text{-S-E}_{34}$, and $\text{S-E}_{34}\text{-S}$.

The additives of E-S-E type were synthesized by the reaction of oligosiloxanediol, $\text{HO}(\text{CH}_2)_2\text{OCH}_2\text{-Si}(\text{CH}_3)_2[\text{OSi}(\text{CH}_3)_2]_k\text{CH}_2\text{O}(\text{CH}_2)_2\text{OH}$, with 2,4-toluylenediisocyanate, followed by the interaction of the resulting macrodiisocyanate with a twofold amount of oligoethylene oxide. The reaction was carried out in chloroform at 60–65°C in a stream of dry argon in the presence of 0.005% tin diethylcaprylate as catalyst. The S-E-S additives were synthesized in a similar way.

Polymer blends of a required composition in a range from 0.015 to 4 wt % additive were prepared by mixing prescribed amounts of dilute tetrahydrofuran solutions of PVC (MW = 82,000) and oligomeric additive. Films for surface analysis were cast from solutions of blends onto stretched cellophane substrate and allowed to air dry for 3 days at room temperature.

The surface composition of the samples was analyzed by X-ray photoelectron spectroscopy (XPS) using a Kratos XSAM-800 spectrometer with a Mg anode at a vacuum of 10^{-9} – 10^{-10} torr. Due to soft operating conditions used for the X-ray gun (75 W, 15 kV, 5 mA), radiation damage to the polymer sample surface during the data collection time was insignificant. To assess the concentration gradient in the near surface regions, the spectra were recorded at two electron takeoff angles, 90° and 50°, corresponding approximately to sampling depths of 50 and 30 Å. Spectra of the pure oligomeric additives, which have a rather high pressure of saturated vapors, were taken at –50°C.

Charge correction in the binding energy scale was made by setting the lowest binding energy feature of the C1s emission to 285 eV. Due to differential charging of the phase-separated surfaces,^{11,12} the signals from PVC showed a slight positive shift (within 0.4 eV) relative to the signals from the oligomeric additive. The magnitude of the shift was determined from the difference between the observed (charge corrected) position of the C12p peak and its "ideal" position in pure PVC (200.7 eV).¹¹ The relative shift of the signals from PVC was taken into account on decomposition of the C1s emission into individual spectral features.

Table I Bulk and Surface DMS Concentrations in Pure Additives (Atom %)

Additive	DMS	
	Bulk	Surface
E ₈ -S-E ₈	51	72
S-E ₈ -S	72	94
E ₃₄ -S-E ₃₄	27	60
S-E ₃₄ -S	54	87

The quantitative analysis of the XPS spectra was made as described in detail in earlier work.² The surface concentrations of PVC and DMS were determined from the integral intensities of the C12p and Si2p signals, respectively. The DU segments manifested themselves in the N1s signal; the EO blocks could be detected from an analysis of the O1s core level.

RESULTS AND DISCUSSION

Table I presents the quantitative results on the pure DMS-DU-EO oligomers. The results show the observed surface concentration of DMS against the known DMS concentration in the bulk. The concentrations are expressed in atomic percent DMS, which shows how many atoms of every 100 nonhydrogen atoms in the neighborhood of a given point belong to DMS (atomic % DMS = 4 × atomic % Si). When applied to the surface layers, this quantity well characterizes the fraction of the sample surface, which is covered with DMS. (Weight percent surface DMS is a less adequate characteristic of the surface coverage because of its dependence on the atomic weights.)

The effect of polymer architecture on the DMS surface segregation in the pure oligomers can be appreciated from Table I by comparing the data for E₈-S-E₈ and S-E₃₄-S. These oligomers have nearly the same stoichiometric concentration of DMS (and exactly the same length of the DMS block). However, S-E₃₄-S, whose DMS blocks are at the chain ends, show a much higher surface segregation of DMS, compared to E₈-S-E₈, with its DMS block in the middle of the chain. As expected, the highest surface concentration of DMS is observed in S-E₈-S, which possesses the highest DMS content and favorable molecular architecture. The lowest surface DMS is found in E₃₄-S-E₃₄, with the lowest stoichiometric content of DMS and unfavorable molecular architecture.

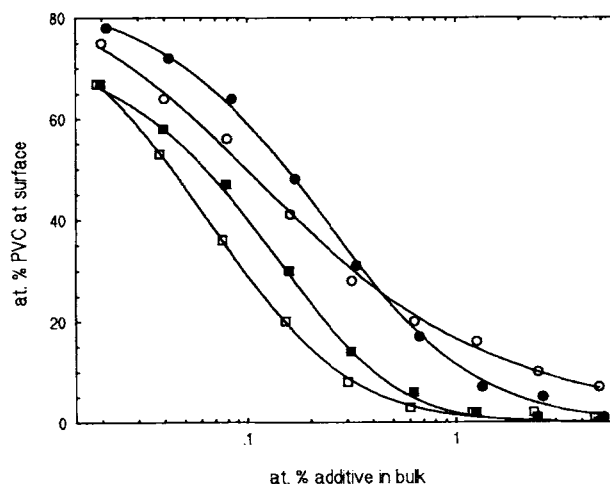


Figure 1 Surface concentration of PVC as a function of the bulk content of additive for blends of PVC with: (○) E₈-S-E₈, (□) S-E₈-S, (●) E₃₄-S-E₃₄, (■) S-E₃₄-S.

The surface behavior of dilute blends of the four DMS-DU-EO oligomers in PVC is illustrated in Figures 1 and 2. Figure 1 shows the surface concentration of PVC as a function of the bulk concentration of the oligomeric additive. The concentrations are given in atomic percent additive defined similarly to that for DMS. So, the curves in Figure 1 provide an idea of the fraction of the PVC surface that remains uncovered with additive. At concentrations up to 0.6 atomic % additive, the effectiveness of the four additives in covering the PVC surface follows the order of their DMS content (see Table I); the higher the DMS content of the additive, the higher the surface coverage of PVC with the additive. At

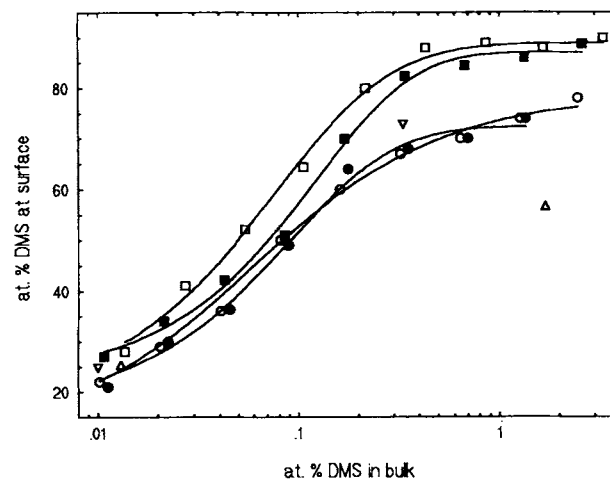


Figure 2 Surface vs. bulk DMS concentrations for blends of PVC with: (○) E₈-S-E₈, (□) S-E₈-S, (●) E₃₄-S-E₃₄, (■) S-E₃₄-S, (△) BAC-DMS, and (▽) MMA-DMS.

high additive concentrations, the additives of S-E-S type provide a nearly complete surface coverage. The efficiency of E_8-S-E_8 is slightly lower; $E_{34}-S-E_{34}$ leaves about 10% PVC surface uncovered.

To follow the effect of the molecular architecture of additive on the DMS surface segregation, the observed surface compositions are to be referred to the same DMS concentration in the bulk. This is done in Figure 2 that shows the DMS surface concentration of the blends as a function of DMS bulk concentration. In the range of higher concentrations (above 0.3 atomic % bulk DMS), the DMS surface segregation is completely governed by the molecular architecture of the additive. The surface/bulk compositional curves for the two additives of E-S-E type are practically coincident, as are the compositional curves for the two S-E-S additives.

The surface behavior of DMS in the higher concentration range is consistent with the expected surface morphology of the blends.² As follows from the results presented in Figure 1, at the high additive contents the additive molecules form a nearly continuous overlayer on the PVC surface. The surface structure of this overlayer is similar to that of the pure additive: the topmost surface region is enriched with the DMS blocks. The extent of surface enrichment is higher for the additives of S-E-S type because of the higher migration mobility of the DMS blocks toward the surface when they are at the chain ends.

The observed difference in DMS surface enrichment between the blends of PVC with the DMS-DU-EO oligomers can also be rationalized in terms of the lamellar morphology model proposed by Chen, Gardella, and Kumler¹ to explain the surface behavior of di- and triblock copolymers of DMS and styrene (PS). According to this model, the free ends of the DMS blocks in DMS-PS-DMS triblock copolymers tend to stretch out to the surface, with the result that the thickness of the outermost DMS dominated layer is nearly equal to the DMS block length. By contrast, in the PS-DMS-PS copolymers, both ends of the DMS blocks are constrained by the PS blocks, so that the DMS block chains in the outermost layer have to be bent over. In this latter case, the thickness of the outermost DMS layer is at least half the DMS block length. If the DMS block length is less than the XPS sampling depth, the DMS surface concentration measured by XPS in the DMS-PS-DMS copolymer will be higher than that for the PS-DMS-PS copolymer. A similar situation can be expected to occur in the overlayers formed by the DMS-DU-EO oligomers on the PVC surface. (Based on the conformational

parameters of the DMS chain, the DMS block length in the DMS-DU-EO oligomers can be estimated to be no more than 40 Å, which is smaller than the XPS sampling depth.)

The DU and EO segments connected with the DMS blocks in the outermost DMS dominated layer segregate to form the next layer enriched with DU and EO. The thickness of this second layer is different in the $n = 8$ and $n = 34$ oligomers. In both cases, however, the DU and EO dominated layer extends to depths considerably greater than the XPS sampling depth. As a result, XPS fails to distinguish between the $n = 8$ and $n = 34$ oligomers to give nearly the same surface compositions (Fig. 2).

We now turn to the range of lower DMS bulk concentrations. An interesting result is that the four concentration curves in Figure 2, corresponding to the four different additives, approach each other as the DMS bulk concentration is reduced. (Thus, at 0.01% bulk DMS the four concentration curves are coincident to within 5 atomic %.) That is, in the lower concentration range the difference in molecular architecture and EO block length between the additives becomes unimportant and the surface segregation of DMS is completely governed by the DMS concentration in the bulk.

Aside from the data for the four oligomeric additives, Figure 2 shows some selected XPS results for two other additives studied previously.^{11,12} One additive is a BAC-DMS multiblock copolymer with the same DMS block length as that in the DMS-DU-EO oligomers ($k = 21$). The other additive is a MMA-*g*-DMS graft copolymer with short DMS grafts ($k = 50$, copolymer C in Gorelova et al.¹²). When added to PVC in amounts corresponding to about 1 atomic % DMS, these copolymer additives provide DMS surface concentrations substantially different from those observed with the oligomeric additives at similar bulk DMS contents. At 0.01 atomic % bulk DMS, however, the results for all additives are very close together. That is, at low DMS contents, the DMS blocks segregate to the surface as if being independent of their chemical surroundings and molecular architecture.

It seems that the observed surface behavior of DMS in the lower concentration range is associated with the transition of the additive molecules in the surface layers from the "thick overlayer" arrangement, with the DMS blocks oriented to the air surface, to the "thin overlayer" arrangement, with the additive molecules oriented preferentially parallel to the surface.²

A good indicator of the orientational changes occurring in the surface layers is the ratio $R = (c_0$

$-c_{\text{Si}})/c_{\text{Si}}$, where c_{O} and c_{Si} are the observed surface concentrations of O and Si, respectively. Inasmuch as PVC contains neither O nor Si atoms, R is unresponsive to the PVC base and well characterizes the organization of the additive molecules at the sample surface. Because the surface concentration of the O atoms entering the DMS blocks is equal to c_{Si} , the difference ($c_{\text{O}} - c_{\text{Si}}$) represents the surface concentration of the O atoms that belong to the other segments of the additive molecules. If the surface consists of pure DMS, then all the observed oxygen belongs to DMS, $c_{\text{O}} = c_{\text{Si}}$, and $R = 0$. As the DU and EO segments appear in the surface layers, c_{O} becomes greater than c_{Si} and R will increase. For all four DMS-DU-EO additives, XPS measurements showed an increase in R as the additive concentration in the blends was reduced. In the high-concentration range, R was equal to 0.3–0.4 for the E-S-E additives and about 0.1 for the S-E-S ones. At a DMS concentration of 0.01 atomic %, R rose to 0.6–0.7. The observed changes in R suggested that the additive molecules in the surface layers did change their arrangement, so that the DU and EO segments became more accessible to XPS.

CONCLUSIONS

The DMS-DU-EO oligomeric additives studied in this work are good surface modifiers of PVC, ensuring a nearly complete surface coverage of PVC at few weight percent modifier. In the range of low additive concentrations, the modifier efficiency is determined by the stoichiometric DMS content of the modifier: the higher the DMS content, the greater the surface coverage of PVC with the additive. At bulk DMS contents above 0.3 atomic %, the surface behavior of DMS in the blends is governed by the molecular architecture of the additive. The additives of S-E-S type, with the DMS blocks at the chain ends, show substantially higher DMS surface segregation, compared to the E-S-E additives, with the DMS blocks in the middle of the chain. The EO block length has no effect on the DMS surface concentration because the EO dominated layer, lying below the outermost DMS dominated layer, extends to depths greater than the XPS sampling

depth. At bulk DMS contents of the order of 0.01 atomic % DMS, all four additives provide nearly the same DMS surface concentration, despite the difference in molecular architecture and EO block length. This result seems to originate from the re-orientational phenomena occurring in the surface layers on the transition of the additive molecules from the thick overlayer arrangement, typical of the pure additives, to the thin overlayer arrangement, with the additive molecules oriented preferentially parallel to the sample surface.

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