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Solvent Effects on Polymer Surface Structure

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Abstract

The surface modification of polymeric materials has been of great research interest in the past few years because of its importance in applications such as biomaterials and coatings. The bulk composition of polymeric materials often cannot provide desired surface properties in these applications. For example low surface energy materials can be obtained via the process of surface segregation. The properties of the solvents used in these processes are critical for surface formation in these polymers. Solvent properties such as polarity, volatility and specific interaction properties with the polymer material are important factors in the process of surface formation. The present paper reviews recent studies of solvent effects in surface segregation in multicomponent polymer systems. Copolymers, polymer blend and multicomponent polymer solution systems are discussed.

Introduction

The surface properties of polymeric materials are critical in many applications, such as wetting, coatings, adhesion, friction, and biocompatibility. (1) Because desired surface properties (e.g. low surface tension or surface energy) are often different from the bulk properties of the material, strategies for modification of the surface composition and structure of polymeric materials have been of great research interest in both theoretical and practical applications in the past couple of decades. (2) Although there are numerous ways to achieve a desired polymer surface, (3-8) surface segregation in multicomponent polymers, including block copolymers and polymer blends, is one process which can involve low cost and high efficiency.

Theoretical studies prove that at equilibrium conditions, low surface energy is the driving force but, practically, it is difficult to achieve complete thermodynamic equilibrium at ambient temperature without specific treatments. Thus, the kinetics of surface segregation are a major factor. (9) Two common approaches to affect kinetics to enhance the surface segregation process are annealing and utilization of selective solvents or solvent mixtures (the subject of the present review). At elevated temperatures, annealing increases the mobility of the polymer segments in the matrix allowing a faster approach to the phase segregation equilibrium state. In some cases, however, it is not practical to use elevated temperatures because of degradation. Studies on solvent effects have shown that solvent properties can influence the kinetic environment of segment migration significantly. The fundamental goal of tuning solvent properties for surface segregation is to alter the kinetic and thermodynamic environment to obtain the desired surface properties of materials without further treatment.

Many surface sensitive characterization techniques have been involved in the study of

surface segregation and interfacial aspects of phase separation. Among these, X-ray photoelectron spectroscopy (XPS) is a widely used quantitative surface analysis technique. It provides surface chemical bonding and composition information on a surface layer of up to ten nanometers, depending on the energy of the X-ray source and the take-off angle of detected photoelectrons. The use of forward recoil spectrometry (FRES) in the studies of interfacial characteristics of polymers was pioneered by Kramer and coworkers (10). It provides direct information about the mass and depth distribution of the target nuclei. Its detection depth is deeper than that of XPS with depth profile information, and the depth resolution of FRES is in the range of 10's of nanometers although a recent report has achieved 6 nanometers over a sampling depth of microns. (11) Attenuated total reflection (ATR)-FTIR is capable of the same order of penetration depth as FRES (a few microns) and is not destructive. (12) While one obtains absolute information on the concentration of components from IR absorption, it is difficult to obtain information on the behavior of molecules on the segmental level. Secondary ion mass spectrometry (SIMS) is a collection of methods for surface and in depth characterization at a much shallower depth (a few atomic layers from the surface), especially with the time of flight technology which extends the mass detection range. Quantitation with SIMS, however, is still limited by the lack of knowledge of ion yields. Ion scattering spectroscopy (ISS), neutron and X-ray reflectivity, surface enhanced Raman scattering, and transmission electron microscopy (TEM) have also been reported in relation to the study of phase separation. Often, multiple techniques are used in a complementary fashion to provide a quantitative picture of surfaces.

While segregation kinetics have significant influence on surface segregation,

experimentally monitoring this process is difficult. To the authors' knowledge, dynamic light scattering is the only technique used in examining the polymer-polymer interaction and polymer-solvent interaction phenomena during solvent evaporation of polymer/polymer/solvent tertiary systems, but investigations have been restricted to polymers with phase separations and without specific interactions. (13-15)

Siloxane-based and fluorine-containing copolymers and polymer blends are two types of multicomponent materials that are widely studied because of the low surface energy component which is often desired for surface properties. Besides the surface energy differences among the components, other factors which influence the extent and rate of segregation are the structure and segment length of the polymer components, molecular weight, molecular architecture and end group effects. (16-18)

This paper will focus on recent studies on polymer solvent interactions and related work in surface segregation and polymer surface modification. The effects of pure solvents, solvent mixtures, solubility and the boiling point of solvents (and therefore evaporation rates) on multicomponent polymer solutions will be highlighted.

Solvent Effects on the Surface Segregation of Copolymers

Thomas and O'Malley (19) pioneered the study of solvent effects on polymer surfaces by investigating the surface composition of films of polystyrene-polyethylene oxide (PS-co-PEO) diblock copolymers cast from different solvents. These examples used pure solvents and first demonstrated solvent effects on polymer surface composition. Their earlier work (20) on these

copolymers reported that varying film-casting solvents had a profound influence on microphase separation and domain formation in the bulk sample morphology. The surface composition dependence on casting solvent was investigated by XPS using ethylbenzene, nitromethane and chloroform as solvents. Of these solvents, ethylbenzene is a preferential solvent for PS, nitromethane is preferential solvent for PEO, and chloroform is a mutual solvent for both components. The copolymers investigated in this study had bulk PS content ranging from 10% to 50% by mole. The solid state surface tension of PS is 36 dyn/cm and PEO is 44 dyn/cm and therefore, it was expected that PS would preferentially segregate at the surface of these materials. It was found that the surface composition of these diblock copolymers varied significantly when cast from different solvents, although they were all enriched in PS. Ethylbenzene cast films resulted in the highest surface concentration of PS. About 70% PS was observed on the surface which the bulk concentration of PS was only 21.4% by molar percentage. As might be expected from solubility considerations, samples cast from nitromethane yielded the least surface segregation of PS among the three solvents. Angle-dependent XPS data also showed composition gradients as a function of depth. Of the three solvents, the mutual solvent for both components, chloroform, resulted in the most pronounced composition-depth gradient. These results demonstrated solvent effects on multicomponent polymer surface composition due to solubility differences. An initial simple model drawn from their results suggested that for pure solvents with similar evaporation rates, good solvents for the component with lower surface tension can minimize the surface segregation due to its preferential solubility.

Solvent mixtures, which can be designed for preferential solubility to certain components

in a multicomponent polymer system, can affect surface segregation and surface composition in a more complicated way. The study of surface composition of diblock copolymers of poly(dimethylsiloxane)-co-nylon-6 (PDMS-co-n6) using mixed solvents exhibits the complex effects of solvent mixtures on surface segregation. Diblock copolymers of PDMS-co-n6 have both amorphous and crystalline morphology (21), a feature shared with PS-co-PEO block copolymers studied by Thomas et al. (19) TEM and wide-angle X-ray scattering (WAXS) results (22) showed that the morphology is very sensitive to processing history, such as the casting solvent and annealing conditions. The morphology of solution-cast films is believed to be determined by the competition between crystallization and microphase separation. When 2,2,2-trifluoroethanol (TFEtOH), which is a good solvent for nylon-6 (n6) but poor for PDMS, is used for casting films, spherical microdomains of PDMS develop with sizes ranging 100-200 nm in diameter. These microdomains are embedded in the crystallized phase. This is likely due to the poor solubility of PDMS in TFEtOH. Although the surface composition is still enriched in PDMS, the formation of microdomains could have prevented the surface segregation from forming an even and continuous homogeneous layer. The addition of toluene to TFEtOH, a good solvent for PDMS, can effectively reduce the formation of PDMS microdomains and favor the crystallization of the polymer. A crystalline layer has been observed and the chemical composition of this layer is close to the bulk composition of the copolymer. A highly segregated surface PDMS layer has been observed by casting from the solvent mixture of 1:2 of toluene/TFEtOH for the diblock copolymer of PDMS-co-n6 with M_n of 3K for PDMS block and 100K for n6 block.

The effect of preferential solvents for polyurethanes was examined by Gardella *et al.*

(23) The use of the solvent mixture of THF and mineral spirits (MS) reveals the solvent volatility has a significant correlation with the extent of surface segregation. Three copolymers of poly(dimethylsiloxane urethane) (PDMS-PU) with PDMS segment molecular weights of 2.4K, 10K and 27K were examined using THF and binary solvent mixtures of THF and MS. THF has a boiling point of 66°C while MS boils at 179-210°C. As THF preferentially evaporates, the increasing concentration of MS in the solvent mixture promotes early precipitation of the hard segment while the soft segment remains highly mobile because MS is a poor solvent for the hard segment in this copolymer. Copolymer structure was also important. The two copolymers with shorter PDMS segments give lower hard segment surface concentration by the binary solvent mixture while the one with longest PDMS segment showed a reverse result. The effect of solvent mixtures on the surface segregation of these copolymer systems is summarized in Figure 1. The curves referred as *B* represent the hard segment surface concentration of films cast from the binary solvent and *A* represent samples cast from pure THF. The shift of peak maximum of curve *B* for different soft segment length indicates the copolymer structure dependence of surface segregation in this binary solvent mixture.

The Hildebrand solvent parameter of solvents is an important descriptor/predictor of polymer-solvent interaction. The correlation of Hildebrand parameters with surface segregation of copolymers was investigated in our lab on the random copolymer of bisphenol A polycarbonate and polydimethylsiloxane (BPAC-PDMS). (24) This study was conducted using pure solvents of carbon tetrachloride, chloroform, methylene chloride, tetrahydrofuran (THF), benzene, and pyridine.

Figure 2 shows the correlation between the extent of PDMS segregation in the topmost

2nm layer of the BPAC-PDMS (50/50) copolymers (25) and Hildebrand parameters of the solvents. In general, it appears that the surface concentration of PDMS increases with the increase of the Hildebrand parameter value of the solvent (the trend of Hildebrand parameter values from carbon tetrachloride to pyridine). However, the surface concentration of PDMS for the sample cast from THF is noticeably higher than that of benzene. This may be understood by the fact that only dispersive and polar forces are considered in Hildebrand parameters while specific interactions such as hydrogen bonding are ignored. Hydrogen bonding cannot be ignored for solvents like THF. The Hildebrand parameter of THF ($18.6\text{MPa}^{1/2}$) is less than that of benzene ($18.8\text{MPa}^{1/2}$), but the hydrogen bonding term (δ_h) of THF by Hansen solubility parameter ($8.0\text{MPa}^{1/2}$) is much greater than that of benzene ($2.0\text{MPa}^{1/2}$); the overall solubility of BPAC-PDMS in THF is actually higher than in benzene.

This result is also considered to be relevant to the effect of solvent volatility on surface segregation process. The solvent volatility affects the surface composition of the casting film in that a highly volatile solvent evaporates quickly, allowing less time for the surface segregation to occur. For example, methylene dichloride has a boiling point of 40°C while pyridine is 115°C . The effect on surface segregation due to fast formation of solid film cast from methylene dichloride can also be examined by annealing the as-cast films and looking for remarkable changes of surface composition due to the failure of solvent-cast films to achieve equilibrium. The results of BPAC-PDMS (35/65%) copolymer cast from methylene dichloride (Figure 3a) shown that the annealing indeed enhanced the surface segregation. When cast from pyridine, which allows longer time for surface segregation before the polymer solution solidifies, annealing did not have a significant influence on the surface composition. The copolymer film of

BPAC-PDMS (35/65%), cast from pyridine, verifies that annealing indeed did not make any detectable change on the surface composition. (Figure 3b)

Solvent Effects on the Surface Segregation of Polymer Blends

The use of blending to modify properties of polymeric materials has seen wide application because of the simplicity in design and process. Using surface segregation as the means of surface modification, polymer blends have advantages over copolymers in that only a very small amount of the surface enriched component is needed. This ensures that the bulk phase properties are not severely changed by the component introduced for surface modification. Polymers used for this purpose are often block copolymers blended to the homopolymer being modified, in which the block copolymer contains a block that is the same as the homopolymer to ensure good compatibility. The other block is the component designed to form the surface. The goal is to use as little of the desired surface forming component as possible and to form an even and complete surface layer with the designed component. Annealing treatments for enhancing surface segregation may not be practical in real applications due to degradation of the polymer or the size or shape of substrates if the polymer blend is used in coatings, therefore the study of solvent effects for enhancing surface segregation in this modification process is considered critical.

PDMS has been extensively studied as a blending compound for its low surface energy. (26,27) Comparison studies of surface segregation behavior of PDMS in polymer blend systems have been conducted extensively in our lab in the past few years (28) The surface PDMS

concentration in diblock copolymers of polystyrene-co-poly(dimethylsiloxane) (PS-co-PDMS) ranges from 80% to 98% by molar percentage for solution cast films from chloroform, (29) while the bulk concentration of PDMS ranged from 34% to 89% by molar percentage. Blending the same diblock copolymer of PS-co-PDMS into homopolymer PS using the same solvent yielded a surface with 94% of PDMS coverage by molar fraction for the bulk PDMS concentration of only 3%. The effect of casting solvent on this diblock copolymer/homopolymer blend system has been examined for different solvents including benzene, methylethylketone (MEK), THF, chloroform, toluene, pyridine and cyclohexane for increasing the surface PDMS coverage without increasing the bulk PDMS concentration. Of these solvents, chloroform and THF are mutual solvents for both components; benzene and toluene are good solvents for PS; MEK and cyclohexane are good solvents for PDMS. XPS data show that there is no significant difference in surface PDMS concentration for samples cast from these solvents if only the topmost layer is concerned (Figure 4) However, angle dependent XPS data show that the concentration-depth gradient of PDMS near the surface varies noticeably. Benzene and MEK cast films give the smallest PDMS concentration-depth gradient while chloroform and toluene cast films resulted in the steepest concentration gradients. This suggests that particularly designed solvent mixtures may alter the surface segregation kinetics by the complex interaction between solvent molecules and polymer segments. For example, by mixing different amounts of toluene (a good solvent for PS but poor for PDMS) to a mutual solvent, chloroform, the surface segregation of PDMS in PS-co-PDMS/PS blend was enhanced to different extents. (30) Figure 5 shows the surface PDMS concentration changes with respect to the solvent composition. The best composition in terms of enhancing surface segregation in this blend system is approximately

30% of toluene by volume. For the blend containing 2% PDMS in bulk, this solvent mixture increased surface PDMS concentration to 97% from 91% as cast from single solvent of chloroform.

Another solvent mixture investigated in the authors' lab that enhances the surface segregation of this polymer blend system was chloroform mixed with a small amount of cyclohexanone. Like chloroform, cyclohexanone is a mutual solvent to both PS and PDMS. But the remarkably high boiling point (165°C) of cyclohexanone make this solvent mixture less volatile. The prolonged volatilization period provides extra time for polymer segments to move around toward its thermoequilibrium point. By our observations, the best solvent composition for this polymer blend surface segregation enhancement is around 5% to 7% by volume. The surface PDMS concentration of PS-co-PDMS/PS blend with 2% bulk PDMS concentration reached 98% by molar fraction. Also, the much flatter depth gradient than that observed by casting from both chloroform and binary solvent of chloroform and toluene suggests that longer volatilization time indeed enhances the segregation process toward its thermalequilibrium.

(Figure 6)

Solvent mixtures for polymer blends have also been investigated by other research groups. For example, J. Quintana and coworkers studied diblock copolymer micelles in solvent binary mixtures. (31) The binary solvent mixture contains a selective solvent for one component in the copolymer, and a precipitant for both components of the copolymer (2-pentanol). It is found that the addition of 2-pentanol caused a slight decrease in solvation, and increase in the micelle molar mass. If a good solvent for both components of the copolymer 2-chlorobutane is added in the binary solvent mixture, the micelle molar mass decreases as the concentration of 2-

chlorobutane increases. (32) This indicates a good solvent increases the activity of polymer segments in the solution while bad solvent decreases it.

By the relationship between polymer solvent interaction parameter and Hansen solubility parameters, it is noticed that hydrogen bonding contributes to the interaction, and consequently influences the phase behavior of polymer blends. Dong and Ozaki (33) observed the miscibility behavior of Poly(4-vinylphenol) (PVPh) and poly(methyl methacrylate) (PMMA) blends. The formation of hydrogen bonds between the two polymers is influenced by the solvent used for preparing the polymer blend. When blend films were cast from tetrahydrofuran solution, only a limited degree of hydrogen bonding interactions is observed, while cast from methyl isobutyl ketone solution shows much more pronounced hydrogen bonding peak. This can be attributed to the strong hydrogen bonding ability of tetrahydrofuran ($\delta_H = 8.0$) which develop hydrogen bonding with polymer molecules, compared with the weaker hydrogen bonding ability for methyl isobutyl ketone ($\delta_H = 5.1$).

Concluding remarks

In this paper, we summarized recent progress in the studies of solvent effects on polymer solution systems and its application in surface modification. A low surface energy polymer block copolymerized to a block with high surface energy has been the major focus point. All the experimental evidence shows that the chemical composition and both chemical and physical properties of the casting solvent have influence on the kinetic process of surface formation. These effects are related with one or more properties or interactions of a polymer solution such as polar force, specific interactions and volatility of the solvent. Although interactions between

solvent molecules and polymer molecule segments on microscale are still far from fully understood, empirical rules can be drawn from the experimental observations. For pure solvents with similar evaporation rates, solvents that are poor for the low surface tension component and good for the other component enhance the surface segregation. For pure solvents of different evaporation rates, those with high evaporation rates can minimize the surface segregation. Mixed solvents have complicated effects on the formation of polymer surfaces of multicomponent polymers, and can be optimized to enhance surface segregation. The progress on the study of solvent polymer interactions has proved that the surface modification of polymeric materials can benefit remarkably from optimizing the solvent for particular polymer blend system and desired surface properties.

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 25. BPAC-PDMS (50/50) stands for the copolymer having a weight percent composition of 50% BPAC and 50% PDMS. Likewise, BPAC-PDMS (35/65) stands for the copolymer having a weight percent composition of 35% BPAC and 65% PDMS.
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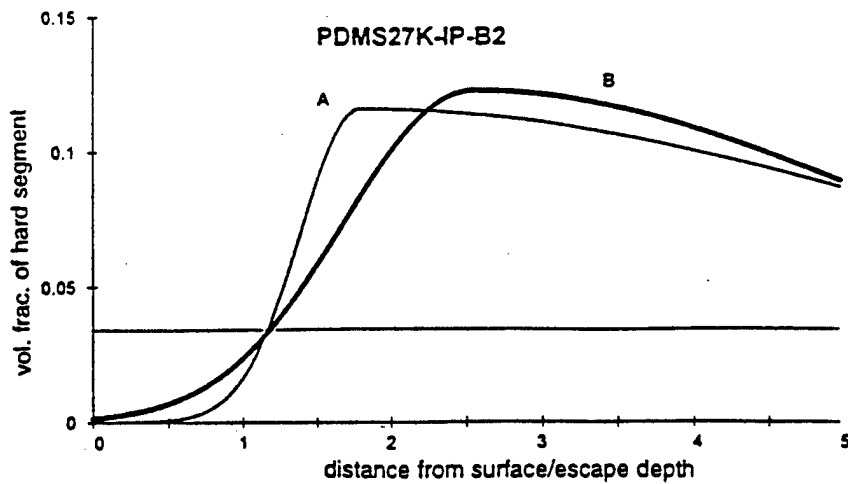
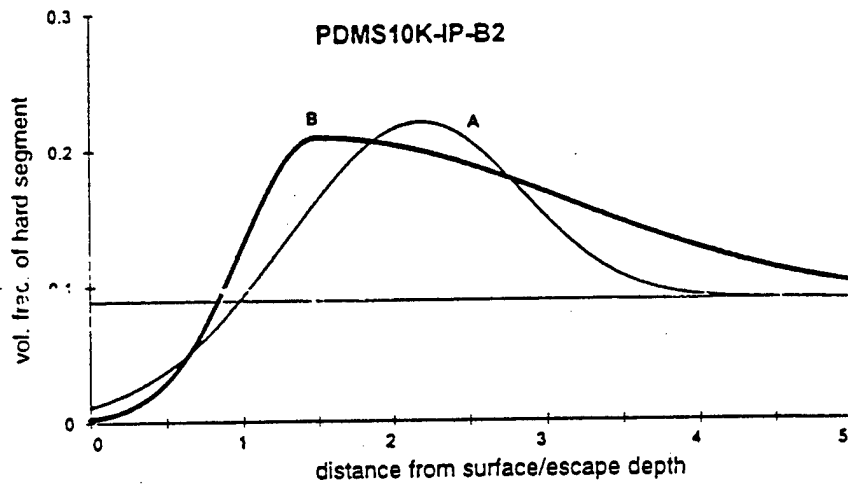
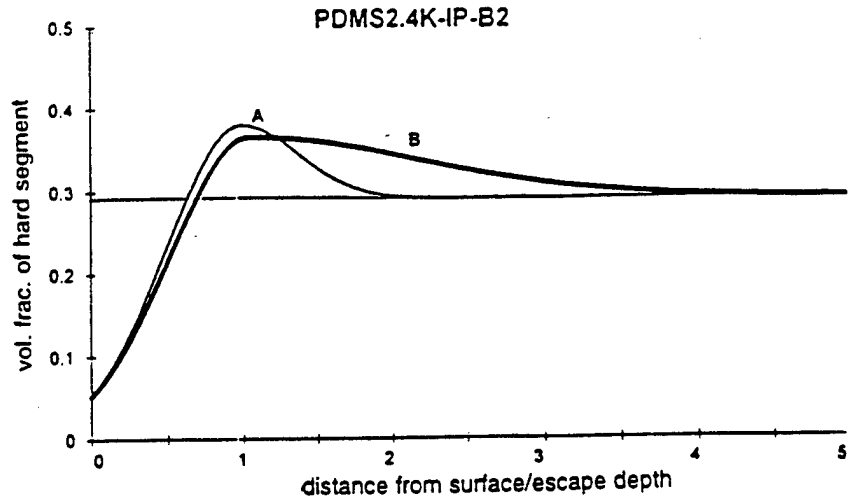
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Figure captions

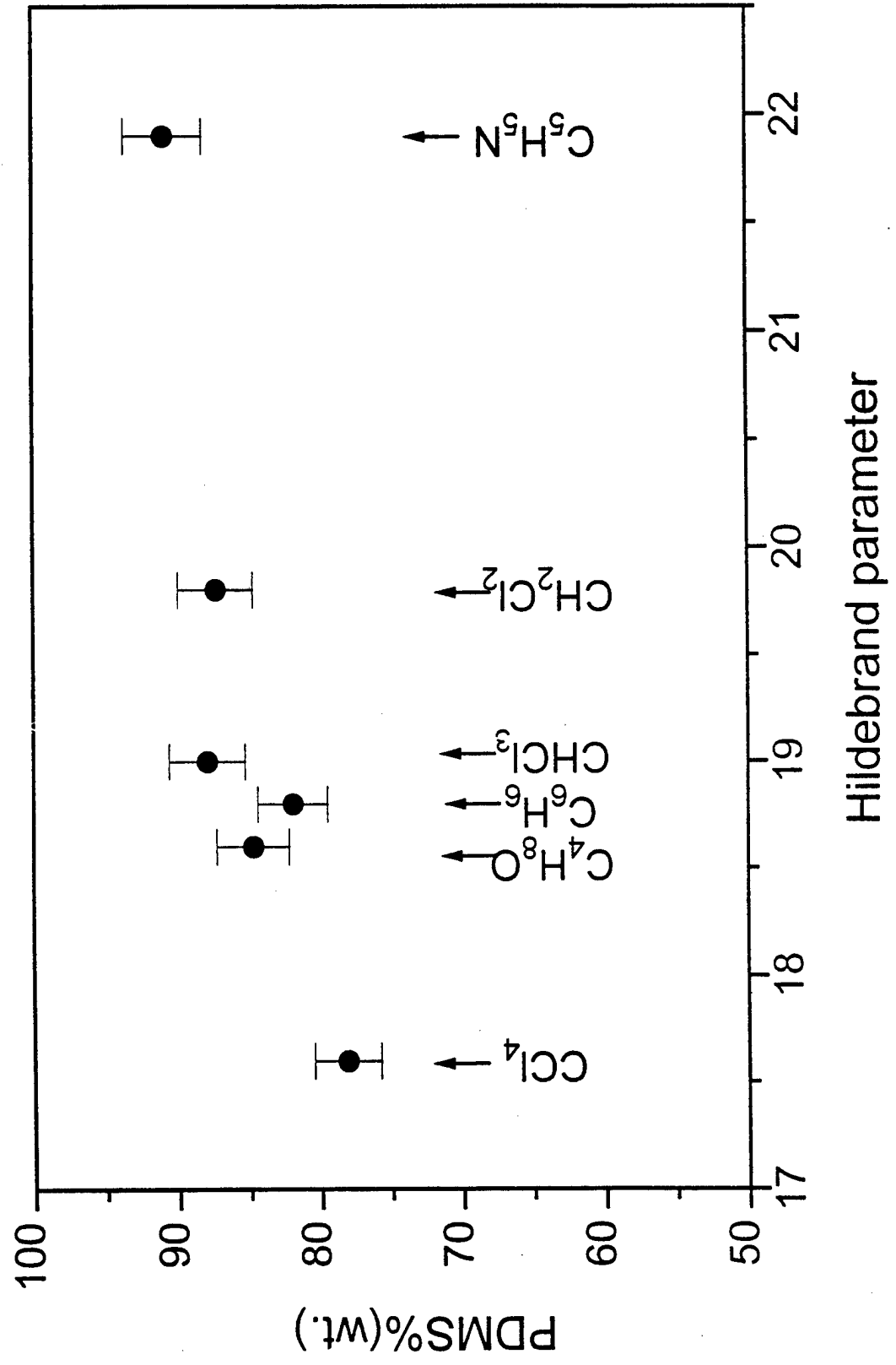
- Figure 1 Concentration depth profiles of the hard segments in copolymers PDMS2.4K-IP-B2, PDMS10K-IP-B2, and PDMS27K-IP-B2. curve A, films cast from THF solutions; curve B, films cast from THF/MS 4/1 solutions. Curves are plotted based on deconvoluted ESCA data. (Reproduced with Permission from Ref. 23)
- Figure 2 Correlation between the surface (in the topmost 18Å) segregation of PDMS in the BPAC-PDMS (50/50) copolymer and the solvent Hildebrand parameter. (Reproduced with Permission from Ref. 24)
- Figure 3 Volatility effect on film formation kinetics. (a) comparison of PDMS surface concentrations between as-cast films and annealed films of the BPAC-PDMS (35/65) copolymer; cast from methylene dichloride; (b) comparison of PDMS surface concentrations between as-cast films and annealed films of the BPAC-PDMS (35/65) copolymer, cast from pyridine. (Reproduced with Permission from Ref. 24)
- Figure 4 Surface DMS concentration on the topmost layer of as-cast films from different solvents by XPS. Bulk DMS concentration 2% by molar percentage. Bnzn: benzene; MEK; methylethylketone; CyHnon: cyclohexanone; CyHn: cyclohexane; Chfm: chloroform; Toln: toluene.

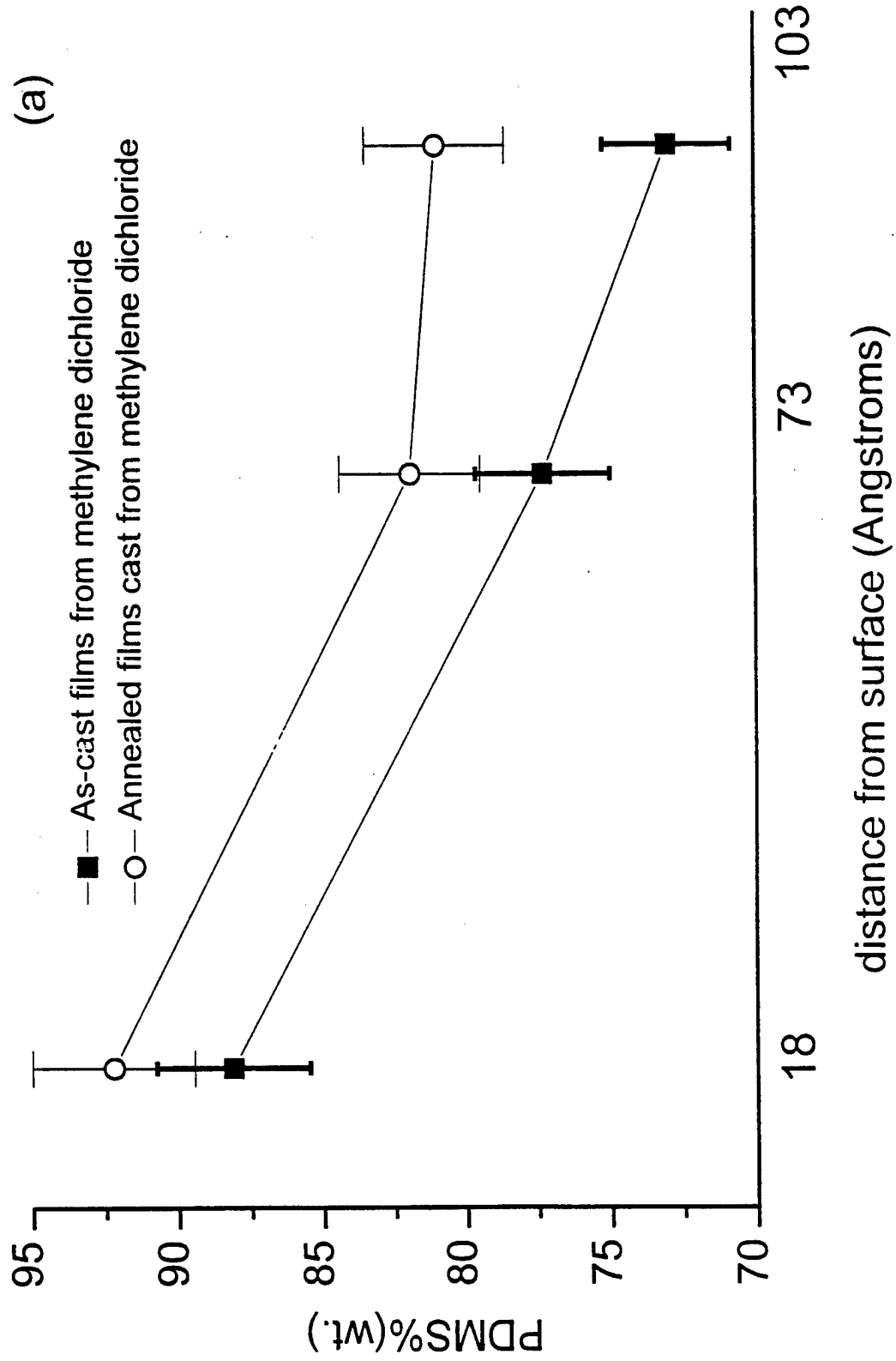
Figure 5 Surface DMS concentration dependence on the solvent composition. As-cast films, 2% bulk DMS concentration. Binary solvents contain 0, 5, 20 and 30 percent of toluene mixed with chloroform by volume.

Figure 6 Comparison of surface DMS concentration by solvents. As-cast films, 2% bulk DMS concentration. Chl: pure chloroform; Tol: binary solvent mixture of 30% toluene in chloroform; Cyclo: binary solvent mixture of 5% cyclohexanone in chloroform.



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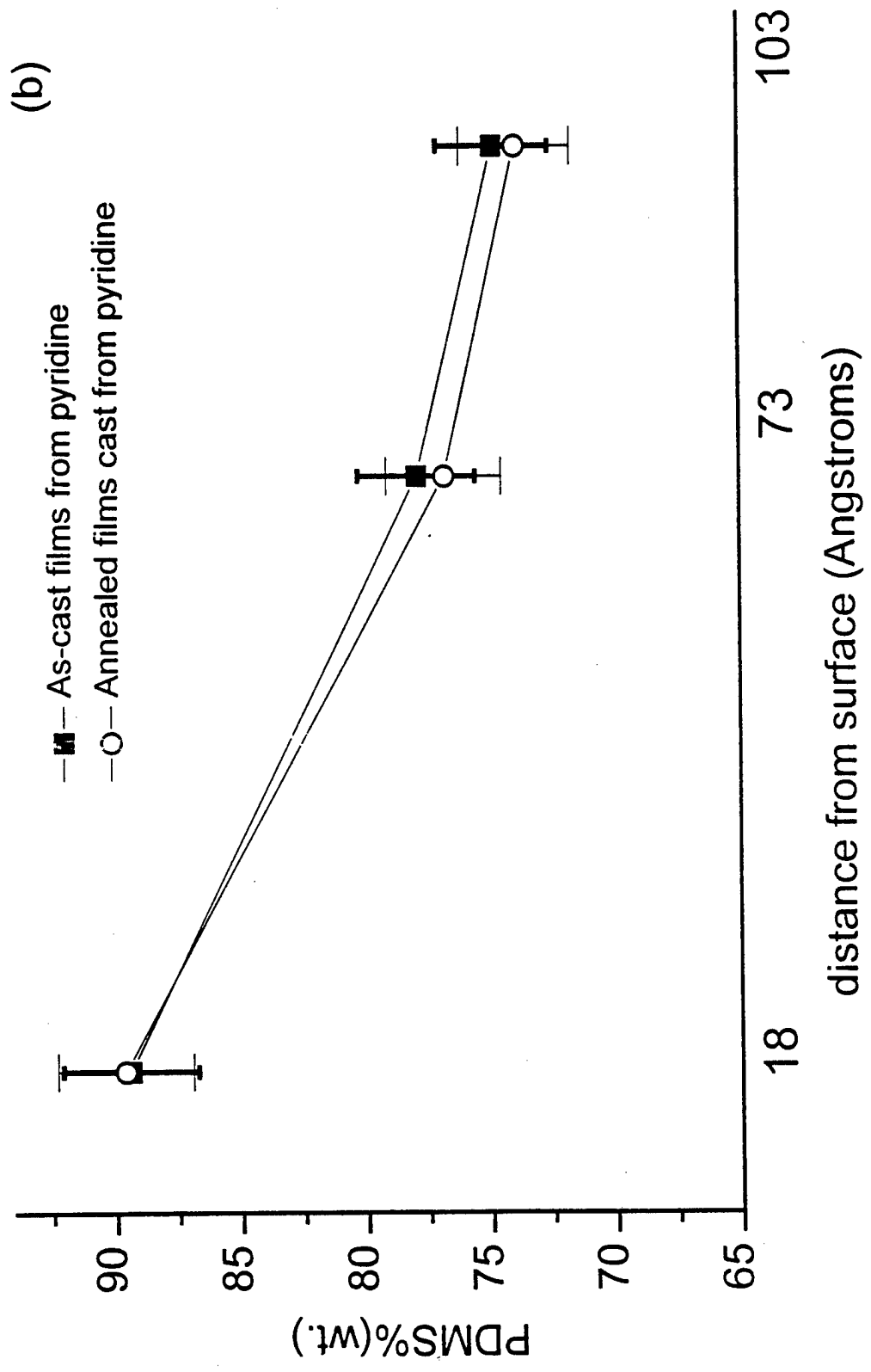
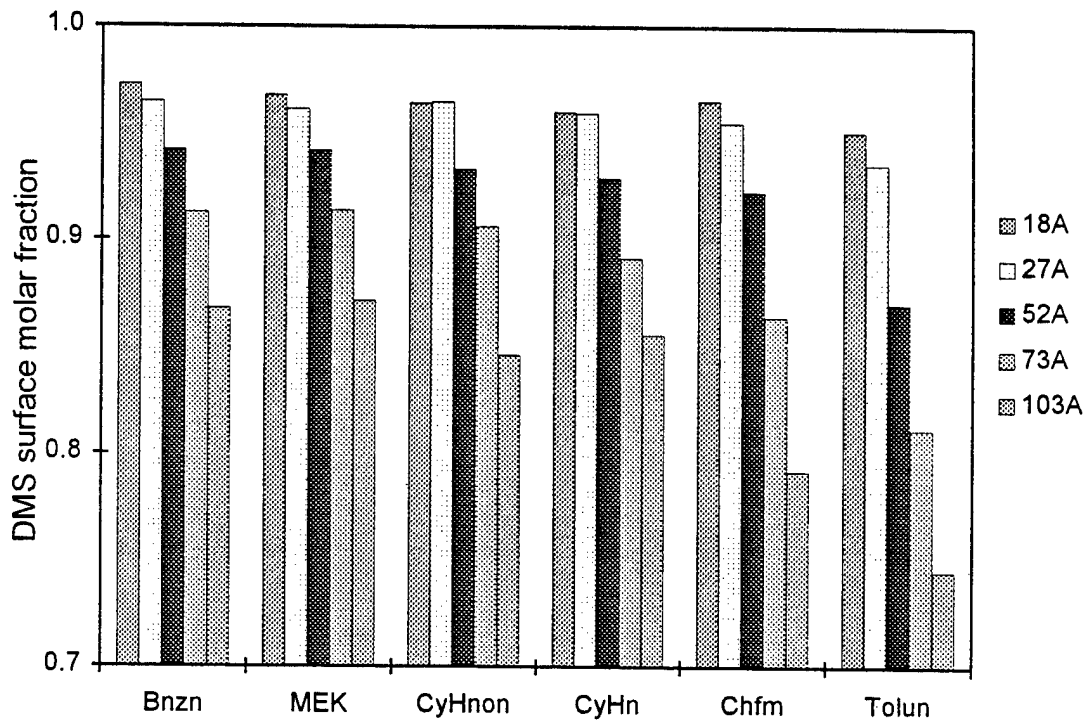
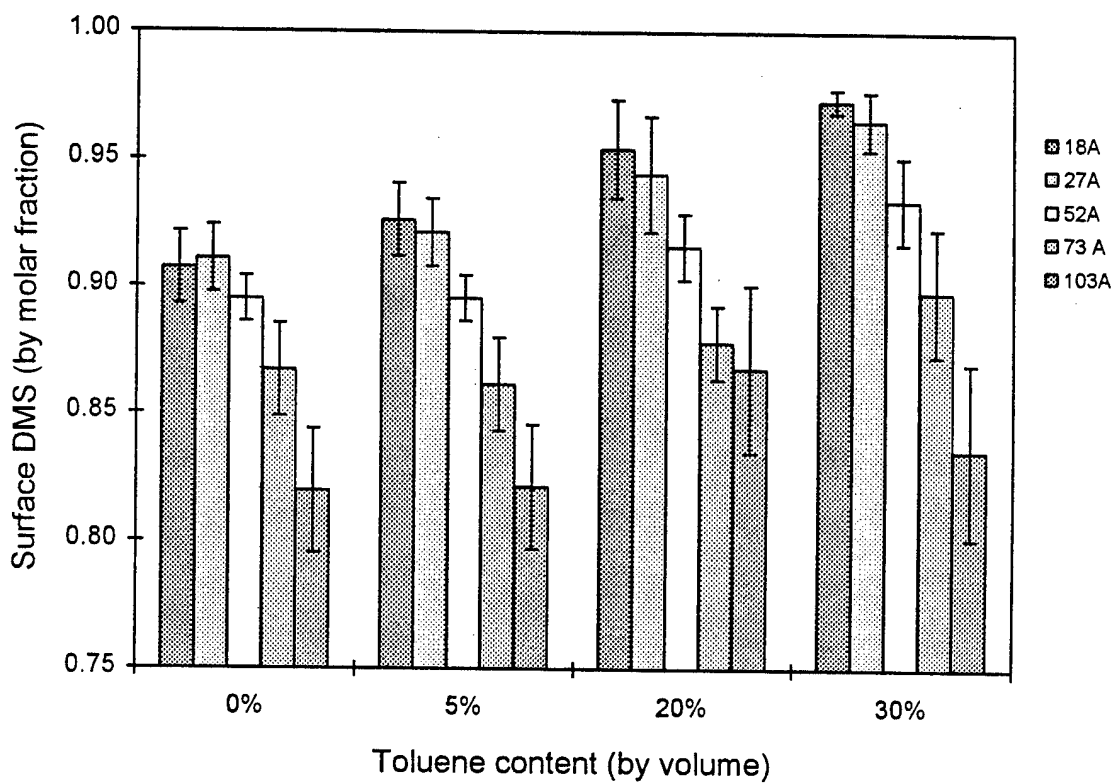


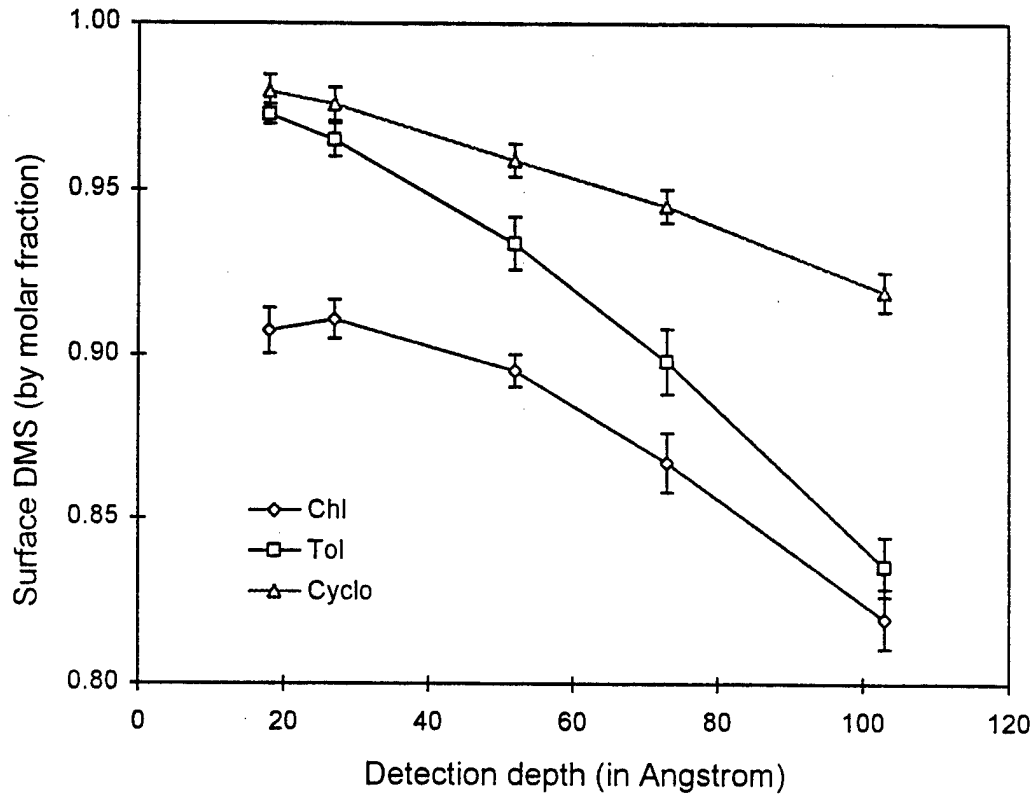
Fig. 3b

Surface DMS by pure solvents, 2% bulk



toluene/chloroform, 2% bulk DMS





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