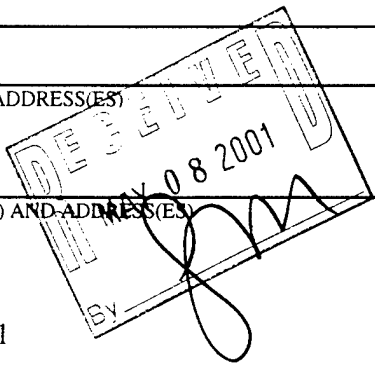


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Microphase Separation and Rheology in Polyurethane Cationomers

Introduction

Polyurethanes are $(AB)_n$ type multiblock copolymers composed of "hard" and "soft" segments that microphase-separate due to thermodynamic incompatibility. The resulting microstructure of low- T_g soft segment-rich domains reinforced by rigid hard segment-rich domains makes polyurethanes excellent thermoplastic elastomers. The degree of microphase separation can be increased dramatically by incorporating a small amount of ionic moieties in one of the segments; such PU ionomers have been demonstrated to have strength and modulus far superior to those of their non-ionic precursors. At high temperatures, polyurethanes are known to undergo microphase mixing into a homogeneous state. Such microphase mixing in di- and triblock copolymers is often accompanied by massive changes in their viscoelastic properties. This correlation between microstructure and viscoelastic properties has not been drawn for polyurethanes due to their chemical instability at high temperatures.

Knowledge of the viscoelastic properties of polymer melts and their dependence on temperature, molecular weight and shear rate is valuable from a melt-processing perspective. Viscoelastic properties also yield fundamental information about the phase behavior of block copolymer melts. Despite this obvious value of rheological data, such rheological studies of PU elastomers have been extremely sparse because commercial PUs flow at fairly high temperatures (over 140°C) and transurethanification reactions cause chemical degradation over the time-scales of typical rheological tests. Clearly, PUs specifically designed for rheological studies must flow at low temperatures (i.e. no crystallinity at high temperatures and low glass transition) and be as thermally stable as possible (i.e. urethanes must be based on aliphatic diisocyanates). Hard segments based on isophorone diisocyanate (IPDI) and 1,4-butanediol (BD) satisfy these criteria by being aliphatic, non-crystalline and with a low glass transition temperature. Several different soft segments of different lengths and degrees of incompatibility with IPDI/BD hard segments were employed to control the degree of phase separation and the resultant effect on rheological properties.

The principle of time-temperature superposition (TTS)¹¹ has proved invaluable in predicting the aging of mechanical properties of polymers over long periods of time. This predictive capability has enabled use of polymers as structural materials, packaging materials, etc. where the expected life of the product is far longer than the time scale of feasible experiments. However, TTS has been shown to fail in many multiphase polymers making it difficult to incorporate aging considerations in designing long term applications. Limited work on PU elastomers has demonstrated the validity of the TTS well below the glass transition of the hard segment. However, these samples were highly elastic (i.e. had non-zero modulus in the terminal region at low frequencies), hence, data at high temperatures at which the polymer flows, are not expected to lie on the low temperature master curves. Preliminary data for amorphous PUs suggest that TTS fails in a systematic fashion, with modulus-frequency data lying on a single master curve at high temperatures, and showing different terminal behavior at low temperatures. It is not at all clear whether this systematic failure will prove useful to predict aging of mechanical properties from high temperature modulus data. This research also investigated the validity of the principle of TTS on model PUs.

Focused Research

There are three principal parameters that govern the properties of polyurethane elastomers: block length N , block incompatibility χ , and composition. This research focussed on materials with 50% by weight of soft segment. Thermally stable polyurethanes with low flow temperatures were synthesized, and the relationship between their microstructure and linear viscoelastic properties were studied as a function of block length and block incompatibility.

Microphase mixing is known to cause massive changes in the viscoelastic properties of block copolymers. Similar microphase-mixing has been observed in polyurethanes but the corresponding changes in

their viscoelastic properties are difficult to study due to their thermal instability. Thermally stable polyurethanes with low flow temperatures were synthesized and the relationships between the structure and the viscoelastic properties were studied.

Differential scanning calorimetry (DSC) and Small-Angle X-ray Scattering (SAXS) experiments demonstrated that the materials changed from homogeneous to microphase-separated as segment length and incompatibility increased. SAXS studies showed a mean field-like approach to the spinodal point with decreasing temperature for some polyurethanes, allowing an estimation of the spinodal temperature.

Dynamic mechanical experiments showed thermorheological simplicity in all materials at high temperature. Unexpectedly, liquid-like terminal behavior was seen even in highly microphase-separated polyurethanes. This is in contrast to other microphase separated block copolymers which usually show non-liquid-like terminal behavior. This difference is attributed to the fact that unlike most di- and triblock copolymers, polyurethanes are incapable of developing long-range order due to large polydispersity in their segment length. Finally, the terminal viscosity and relaxation time were found to strongly depend on segment length, with power law exponents of about 5.

Major Results

Microphase mixing

From DSC data, the I-725 series show a broad glass transition at a temperature intermediate to that of the pure hard and soft segments. The I-1000 series exhibit two poorly resolved glass transitions, followed by a distinct endotherm at about 60°C. Similarly, though somewhat more intense, endotherms are found in I-2000 series. The mechanisms responsible for these endotherms are not well understood, but they are highly sensitive to thermal history. Annealing at 55°C overnight completely erases the endotherm. Qualitatively, the unquaternized materials show a decrease in T_g as block length increases indicative of better microphase separation. Within each series, the T_g does not change significantly with increasing quaternization, except in the I-1000 series where the T_g becomes better defined. This is somewhat surprising since more quaternization is expected to improve microphase separation and hence lower the T_g . However, there is a competing effect: as quaternization increases, the T_g of the pure hard segment increases as well. Since some hard segment is usually dissolved in the soft-segment-rich phase, it causes the T_g of the soft segment phase to increase. Evidently, this is enough to offset the lowering of T_g due to better microphase separation. This also implies that the I-725 series is not completely homogeneous. The following equations were used for quantitative thermal analysis.

$$T_g = \frac{w_{ss} T_{g,ss} + \alpha w_{hs} T_{g,hs}}{w_{ss} + \alpha w_{hs}}$$

$$\Delta C_p = w_{ss} \Delta C_{p,ss} + w_{hs} \Delta C_{p,hs}$$

$$f_{ss} = \frac{\alpha(T_{g,hs} - T_g)}{(T_g - T_{g,ss}) + \alpha(T_{g,hs} - T_g)}$$

$$F_{ss} = \frac{\Delta C_p}{f_{ss} \Delta C_{p,ss} + (1 - f_{ss}) \Delta C_{p,hs}}$$

where $T_{g,ss}$, $\Delta C_{p,ss}$, $T_{g,hs}$, and $\Delta C_{p,hs}$ are the glass transition temperature and change in heat capacity at the glass transition of the pure soft and hard segments, respectively, T_g and ΔC_p are the corresponding properties for the soft-segment-rich phase of the polyurethane, and $\alpha = \Delta C_{p,hs}/\Delta C_{p,ss}$. f_{ss} is the weight fraction of the soft segment in the soft-segment-rich phase, and F_{ss} is the weight fraction of soft-segment-rich phase. w_{ss} and w_{hs} ($=1 - w_{ss}$) are the overall weight fractions of the soft and hard segments in the polyurethane and are close to 50% for all the materials. Quantitative analysis indicated that the soft-segment-rich phase in the I-2000 series is fairly pure ($f_{ss} \sim 0.8$) although the weight fraction of this phase is relatively small (~ 0.2). Since a well-defined hard segment T_g is not visible, the fraction of the hard-segment-rich phase F_{hs} must also be small. The overall composition is close to 50% soft segment, and hence a large fraction of this material must reside in the interface between the lamellae and undergo a glass transition at temperatures between the T_g and $T_{g,hs}$.

Most of the polyurethanes studied showed no significant change in their scattering patterns with temperature. However, two polyurethanes showed a decrease in scattering intensity with temperature which

was ascribed to microphase mixing (scattered intensity is proportional to the square of the electron density fluctuations in the material). One of these samples is shown in Figure 1 in which the decrease in peak intensity with increasing temperature is clearly evident. These data were analyzed on the basis of the mean field theory that predicts an approach to the spinodal temperature for the instability of the homogeneous sample as

$$\frac{1}{I} \sim \text{const} \tan t - 2\chi N_0 \sim k_1 + \frac{k_2}{T} \quad 1$$

where χ is the Flory-Huggins parameter and I is the intensity scattered at temperature T . This is shown in the inset to Figure 1 where the spinodal temperature is found to be about 14 C. To our knowledge, this is the first time that graphs such as Figure 1 have been drawn to demonstrate the applicability of mean field theory for any multiblock copolymer.

Effect of segment length

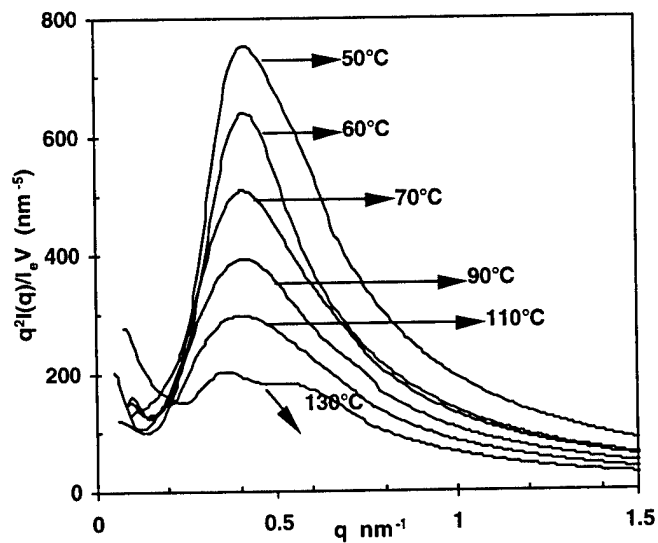
A series of polyurethanes with polyester soft segments were synthesized with varying block length, but fixed composition and segmental incompatibility. DSC data indicate that microphase separation increases with block length (I-725 series was almost homogeneous, whereas the I-2000 series was almost completely microphase separated). A comparison of SAXS patterns of the three I-series (I-725, I-1000 and I-2000) shows that long spacing increases with block length. Linear dynamic mechanical properties of these polyurethanes were studied as a function of frequency and temperature. These were fitted to the Rouse equations and the corresponding terminal relaxation properties (i.e. characteristics of the slowest relaxation processes) were obtained. Figure 2 shows a result of this work viz. the terminal viscosity as function of block length. Clearly, viscosity is very strongly dependent on block length with an apparent power law exponent of about 5.

Effect of segmental incompatibility

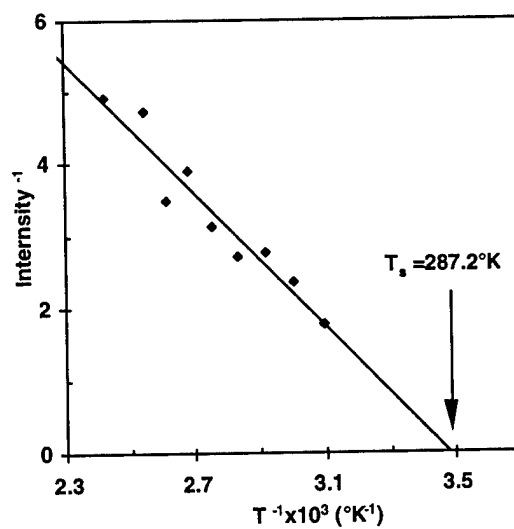
The segmental incompatibility was varied by the extent of quaternization. There is no appreciable change in the T_g upon changing the extent of quaternization (i.e. block incompatibility) revealed by DSC traces. SAXS experiments showed that quaternization causes an increase in the scattering intensity in SAXS experiments, a decrease in peak width, and a decrease in the peak position, especially at low quaternization; the latter corresponds to an increase in the long spacing. This indicates that increasing incompatibility causes chain stretching. High-temperature scattering experiments were also performed on these materials. All samples (except I-725-12, I-2000-0) showed no major change in scattering with temperature up to 130 °C, except for a slight increase in long spacing d . It should be noted that block incompatibility increases with decreasing temperature. The direction of the shift in d is consistent with the interpretation that, in block copolymers with polydisperse blocks, increasing incompatibility causes successively shorter blocks to microphase-separate and decrease d . However, the increasing incompatibility with quaternization contradicted this expectation by causing d to increase significantly. We have no explanation for this contradictory behavior upon increasing χ by decreasing temperature in one case and increasing quaternization in the other case. One possibility is that increasing quaternization has effects other than simply increasing block incompatibility.

Increasing quaternization also causes an increase in storage modulus at high temperatures and a correspondingly higher temperature for flow. This increasingly solid-like behavior with quaternization has three distinct causes that have been described briefly by Hamersky et al.. The first cause for the increasingly solid-like behavior is "bare" effects, i.e., those effects that are not related to microphase separation. In addition to the bare effects, the viscoelastic properties of the present materials are influenced by microphase separation in two qualitatively distinct ways. The first of these is important when one of the components has a much higher monomeric friction coefficient than the other. In such a case, microphase separation causes the local composition to deviate from the average composition, and hence the local monomeric friction coefficient also varies throughout the sample. This will be referred to as the "dynamic asymmetry" effect of microphase separation. The second effect of microphase separation is the "thermodynamic" aspect, which is the energy penalty of dragging a hard segment through the soft-segment-rich microphase, and vice versa. This energy penalty, which also impedes chain motion and thereby increases the viscosity, is independent of the relative friction coefficients of the two blocks.

At sufficiently high temperatures, TTS is seen to work for all materials in the experimental frequency range. The master curves may be described almost quantitatively using Rouse theory. In general, increasing quaternization is seen to increase both the terminal viscosity and the terminal relaxation time of polyurethanes. At lower temperatures, a failure of superposition is seen for materials with large block length or large block incompatibility. It is also observed that as quaternization increases, superposition fails at successively higher temperatures. Such failure of superposition has often been demonstrated to be due to an ODT or due to composition fluctuation. Since our SAXS experiments show almost no change with temperature, the failure of superposition of the cationomers cannot be attributed to microphase mixing. It is believed that this failure is due to proximity to the T_g of the hard-segment-rich microphase, because time-temperature superposition is not expected to apply so close to the T_g .



(a)



(b)

Figure 1 Scattering patterns of a polyurethane. (a) Decreasing scattering intensity with increasing temperature corresponds to microphase mixing. (b) shows a quantitative analysis of the decrease in total intensity, and the corresponding mean field estimate of the spinodal temperature.

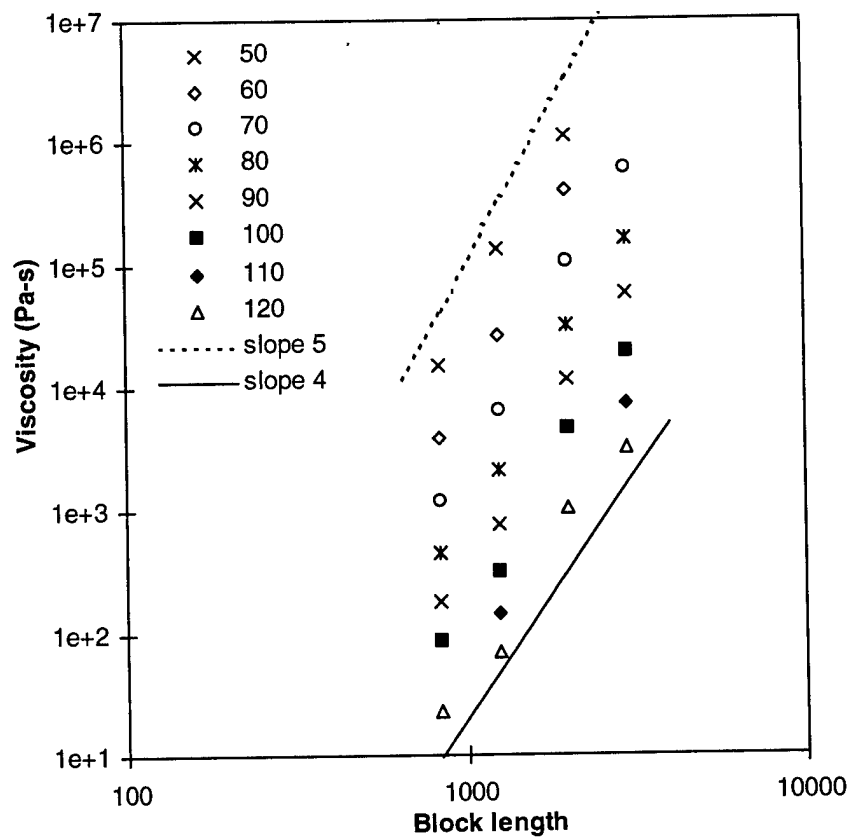


Figure 2 Effect of segment length on the terminal viscosity of polyurethanes.

Quaternary Ammonium Functionalized Poly(propylene imine) Dendrimers as Potent Biocides

1 Introduction

Dendrimers are well defined, highly branched macromolecules that emanate from a central core.¹⁻⁴ While there have been many advances in dendrimer synthesis, application of these novel materials has lagged behind. Since the novel dendritic architecture brings a very high number of functional groups in a compact space, it is reasonable to expect that these novel molecules will play a major role in materials whose performance depends on high local concentration, such as drugs or antimicrobial agents. Presently, there are few reports in this field. The purpose of this study was to synthesize novel dendritic biocides by converting the surface groups of DSM Astramol™ poly(propylene imine) (PPI) dendrimers to quaternary ammonium functionality and to test their biocidal capability. Quaternary ammonium compounds (QACs) have been widely used as disinfectants.⁵ The target biocides not only carry up to 64 quaternary ammonium groups per molecule but also possess a polycationic structure, which is well known to increase the permeability of cell membranes and thus aid the killing process.

2 Materials and Methods

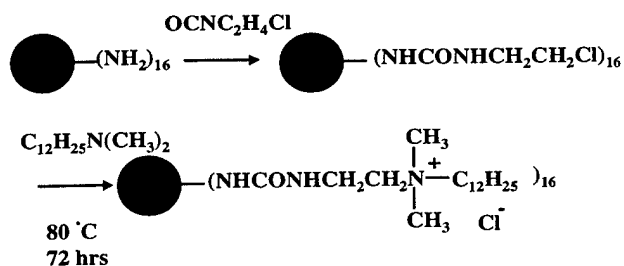
Hyperbranched polymers with hydroxyl groups at their periphery were donated by Perstop Inc. Poly(propylene imine) dendrimers with primary amine end groups, 2-chloroethyl isocyanate and dimethyl alkyl amines (C₈, C₁₂, and C₁₈) were obtained from Aldrich.

Recombinant *E. coli* strains containing a fusion of *Escherichia coli* heat shock promoters and the *lux* gene of *Vibrio fischeri* were developed at Dupont.⁶ Whenever the bacteria receive stress from a toxic compound, the intensity of light emitted from the bacteria will change. From the "light-on" or "light-off" response one can obtain real-time cell viability data. Strain TV 1048, in which the *lux* operon is coupled to the promoter of *lac* operon, was used in this study. Bioluminescence is observed under normal growth conditions. Whenever the bacteria are in a biocidal environment, the light-off response quantitatively corresponds to the toxic effect of the biocide.

The medium used for TV1048 was Luria-Bertani (LB) supplemented with 25 µg/ml kanamycin monosulfate to maintain the plasmid. The plasmid-containing strains were grown to the early exponential phase at 30 °C and then mixed with a known amount of the test sample. Bioluminescence was measured using a luminometer (Model 20e, Turner Design, CA).

3. Results

To synthesize dendritic biocides, the peripheral hydroxyl groups of the hyperbranched polymers and the primary amine groups of PPI dendrimers were reacted with 2-chloroethyl isocyanate to yield pendent chloroethyl groups. These end groups were then quaternized by tertiary amines such as dimethyldodecylamine (Scheme 1. The filled circle represents a complete dendrimer molecule except the end groups.). An example of the nomenclature used is D3CINC12, which denotes dimethyldodecyl (C12) ammonium (N) chloride (Cl) functionalized PPI generation 3 dendrimers (D3). These materials were characterized by elemental analysis, ¹H and ¹³C NMR, FTIR and Gel Permeation Chromatography (GPC).



Scheme 1 Synthesis of dimethyldodecyl ammonium chloride functionalized PPI generation 3 dendrimers

The antibacterial properties of these novel biocides against Gram-negative *E. coli* were determined by a bioluminescence method (Figure 1). The result was expressed as the bioluminescence normalized to a control (without biocide) vs. time. The reduction of luminescence quantitatively shows the antibacterial properties of the sample. At 4 µg/ml, the biocide inhibited the growth of *E. coli*, but the bacteria could still adjust to the environmental stress and survived. At higher concentrations (20 µg/ml), the bioluminescence decreased very rapidly and went down to undetectable levels in 15 minutes indicating a strong biocidal effect.

To quantify the level of the biocidal effect of these samples and to compare it to their small molecule counterparts, EC₅₀ was determined. EC₅₀ is the concentration of the compound, which causes a 50% reduction in the

bioluminescence. A lower EC_{50} indicates a more toxic compound. EC_{50} of D3CINC12 is about 12 $\mu\text{g/ml}$ at 5 minutes while EC_{50} of trimethyldodecyl ammonium chloride is about 2000 $\mu\text{g/ml}$ at 5 minutes. The dendrimer architecture increases the potency of QACs against *E. coli* over 100 times.

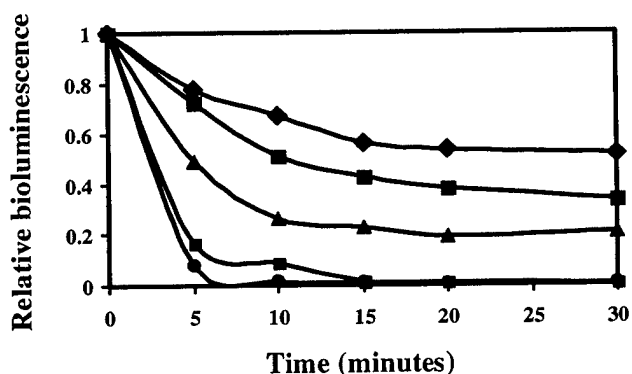


Figure 1 Time-course of bioluminescence of *E. coli* in contact with D3CINC12 (diamond 4 $\mu\text{g/ml}$, rectangle 8 $\mu\text{g/ml}$, triangle 12 $\mu\text{g/ml}$, cube 16 $\mu\text{g/ml}$ and circle 20 $\mu\text{g/ml}$)

Conventional linear or branched polymeric QACs are commercially available. Interestingly, not enhanced efficiency but low toxicity to humans and the absence of foaming are often cited as their special features.⁹ Conventional polymeric QACs are about the same or less potent than their small molecule counterpart depending on different chemical structures. Therefore, the increased potency of dendritic biocides does result from the novel dendritic architecture. These biocides could possibly achieve enhanced antimicrobial properties, low toxicity and the absence of foaming together. The significant improvement of the biocidal action of dendritic biocides can be attributed to the high number of functional groups in a compact space and the polycationic structure. QACs are not very effective on Gram-negative bacteria such as *E. coli* because they have a very sophisticated outer membrane structure that effectively keeps out the antibacterial agents. The combination of the high functional group density and the increasing permeability due to the polycationic structure, making it easier for dendritic biocides to reach and disrupt cell membranes which eventually leads to cell death.

The effect of the hydrophobic chains on the biocidal activity was also investigated (Figure 2). Dendritic biocides with C12 chains tended to be the most effective, followed by C18 chains. Those with C8 chains were the least active of the three. The difference could be explained by the hydrophobicity of the chains. Longer hydrophobic chains will be more effective in disrupting cell membranes to kill the bacteria while they also have a lower cell wall permeability.

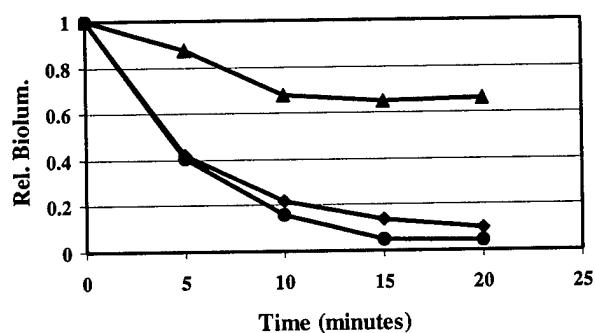


Figure 2 Effect of chain length on biocidal activities (triangle D3CINC8, diamond D3CINC18, and circle D3CINC12. The concentration is 12 $\mu\text{g/ml}$.)

The dendrimer generation dependence showed very complicated behavior (Figure 3). However, the trend in biocidal activity of D5CINC12 > D4CINC12 > D1CINC12 > D2CINC12 > D3CINC12 held for an extended period of time. Dendritic biocides from generation 5 turned out to be the most potent while those from generation 3 the least. The higher the generation, the greater the number of quaternary groups, so the more potent it should be. However, if the permeability of these biocides through the cell membrane is considered, the trend should be the opposite. Both of these effects create a complicated response. It appears that larger dendritic biocides with more functional groups are more potent at longer times.

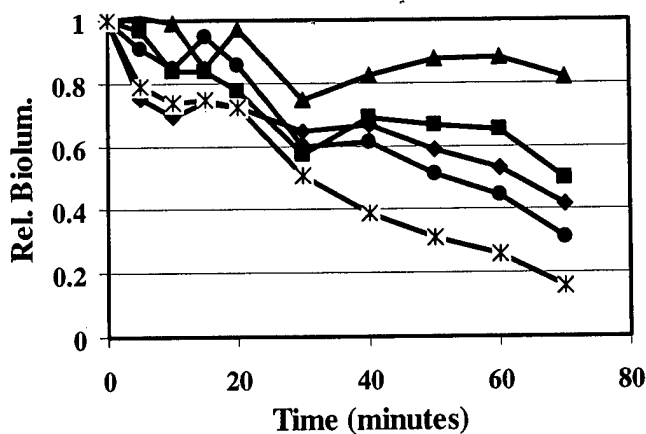


Figure 3 The effect of generation on biocidal activities (triangle D3CINC12, rectangle D2CINC12, diamond D1CINC12, circle D4CINC12, and star D5CINC12. The concentration is 12 $\mu\text{g/ml}$.)

Finally the difference between dendrimers and hyperbranched polymers was also studied (Figure 4). It is very important since hyperbranched polymers are less expensive and considered good substitutes for dendrimers in industrial applications. Results from samples with the same number of functional groups of dendrimers (PPI generation 4) and hyperbranched polymers (Perstop generation 3) showed that biocides from dendrimers were more potent, which can be explained by the fact that dendrimers are more compact and therefore have higher permeability through the cell membrane.

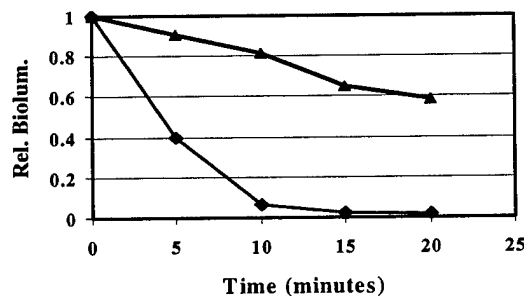


Figure 4 Biocides from PPI dendrimers (diamond D4CINC12, 12 $\mu\text{g/ml}$) are more potent than those derived from Perstop hyperbranched polymers (triangle H3CINC12, 12 $\mu\text{g/ml}$)

To verify that the biocidal effects of D3CINC12 were not bacteria dependent, its antibacterial properties against Gram-positive bacteria *Staphylococcus aureus* were investigated by suspension tests. Results in Figure 5 showed that D3CINC12 could inhibit the growth of *S. aureus* as low as 1 $\mu\text{g/ml}$ and effectively kill them at 10 $\mu\text{g/ml}$ in 60 minutes, which demonstrated its potency on typical Gram-positive *S. aureus*.

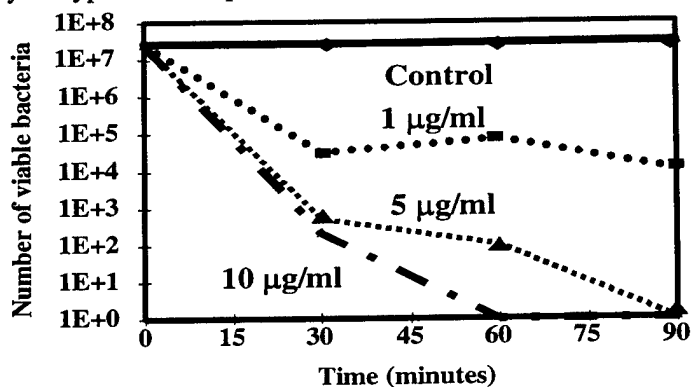


Figure 5 Biocidal effect of D3CINC12 on *S. aureus* in a suspension test

We have demonstrated that it is feasible to synthesize highly potent dendrimer based antibacterial agents. These novel dendritic biocides were shown to be over two orders of magnitude more potent than their small molecule counterparts, which clearly proved the advantage of dendrimers over small molecules. The dendritic architecture could be considered having the ability to greatly increase the effectiveness of common cationic disinfectants.

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List of all publications and technical reports supported under this grant or contract.

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8. Sachin Velankar and S.L. Cooper, "Melt Studies of Multiblock Polyurethane Elastomers", Conference of the American Physical Society, Spring 1997.

List of all participating scientific personnel showing any advanced degrees earned by them while employed on the project

Philip Jackson (Graduate research assistant)

Garland Fussell (Graduate research assistant)

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Shaun Ramsey (Undergraduate research assistant)

Report of Inventions (by title only)

Quaternary ammonium functionalized dendrimers: their preparations and applications as potent biocides thereof, (patent pending)