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Silver doped antibacterial polyamidoamine side chain dendritic polyesterurethane (SCDPEU) architectures

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Abstract The antibacterial activities of side chain dendritic polyesterurethane (SCDPEU) as well as its silver doped structures were studied against *Escherichia Coli* bacteria. The results showed that the silver doped structures attain high anti-bacterial activity. Formation of silver doped side chain dendritic polymers was investigated from the UV-vis plasmon absorption band of silver particles.

Introduction

Polyamidoamine (PAMAM) dendrimers [1–3] have recently attracted increasing interest as biocompatible macromolecules for biomedical applications. In particular, there is considerable current interest in the development and use of dendronized polymers/side chain dendritic polymers (SCDPs) for biomimetic applications. Polyurethanes have recently been of increasing interest for biomedical applications [4] such as mammary prosthesis, vascular catheters, artificial skin, vascular grafts, artificial heart diaphragms and valves as well as many other types of tissue and blood contacting materials. Side chain dendritic polyurethanes [5] represent a class of polymers that appears to be used for the development of a wide range of essentially important biomaterials with many potential functions. Also, in the field of biomedical polymeric materials infections associated with the biomaterials represent a significant challenge to the more wide spread applications of medical implants. In this context, we have very recently shown [5] that the silver doped polyamidoamine side chain dendritic polyurethane (SCDPU) architecture exhibited the antibacterial activity. Motivated by this approach we wish to report herein the antibacterial activity of our recently developed sebacic acid embedded side chain dendritic polyesterurethane (SCDPEU) [5c] and its complexes with metal ions, especially the silver ion. Since sebacic acid is an important biocompatible building block, it appears, therefore, that the polyurethane of this type may have improved biocompatibility compared to SCDPU. In addition, sequestering of silver particles by this polyurethane would allow us to develop antibacterial SCDPEU with enhanced biocompatibility.

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Experimental

Materials

Side chain dendritic polyesterurethane (SCDPEU) was synthesized as described previously [5c]. Silver nitrate, sodium borohydride, nutrient agar and other reagents were used as received.

Preparation of silver doped (Ag^+/Ag^0) polymers of SCDPEU

Synthesis procedure of silver doped polymers is similar to those reported [6–8] procedures. The SCDPEU (1) encapsulated silver particles were synthesized in DMSO: H_2O (1:1) solution containing equal volume of SCDPEU (1.69×10^{-3} M) and $AgNO_3$ (3.68×10^{-2} M). After allowing the solution to equilibrate for 20 min, $NaBH_4$ was added to reduce the silver ions. The reduction of silver ions was checked by SHIMADZU UV-vis spectrophotometer.

Antibacterial assessment

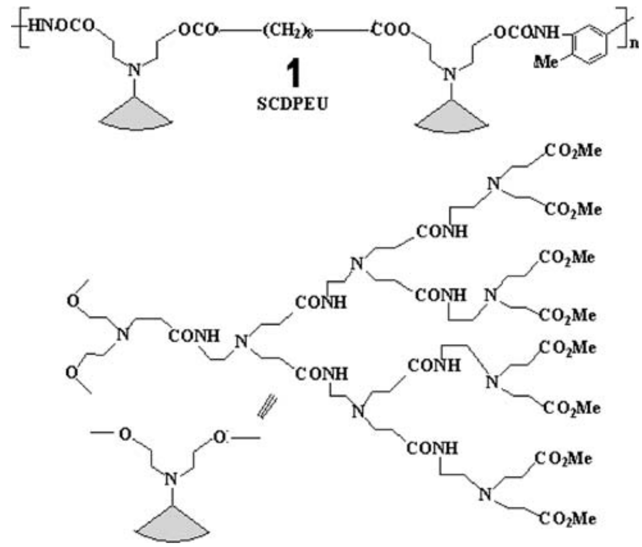
The anti-bacterial activities of SCDPEU and its silver doped products were determined against *Escherichia coli* bacteria using nutrient agar method. A mixture of nutrient broth (13 g) and nutrient agar (15 g) in 1 liter distilled water at pH 7.2 as well as the empty Petri-plates were autoclaved. The agar medium was then casted into the petri-plates and cooled in laminar airflow. The assay plates were then seeded with *Escherichia coli* bacteria. 20 μl of each of the prepared sample solutions was taken in each of the whatman paper discs (6.5 mm dia.). The discs loaded with samples were planted onto the agar plates. All the plates were incubated at 37 °C for 18 h and were examined if a zone of inhibition had been produced around sample-loaded discs.

Results and discussion

Characterization of Ag^+/Ag^0 doped polymers (SCDPEU)

The synthesis of polydendron **1** used was described in our previous paper [5c] and structurally represented in Scheme 1. The choice of sebacic acid component as incorporated into the main chain may enable to obtain the polydendron **1** with enhanced biocompatibility.

A key feature of this polymer is the dense functionalities in its architecture allowing to be effective attribute to host silver particles. The characteristics of the resulting silver doped composites derived from SCDPEU **1** were estimated on the basis of UV-vis spectroscopic measurement. On addition of $NaBH_4$ into the solutions, silver particles were formed resulting in the immediate change in solutions colour from light yellow to orange. Before reduction, solution of Ag^+ ion doped SCDPEU exhibits no absorptions in the UV-vis spectra due to the d^{10} configuration of silver ions. However, zero-valent silvers are known to have intense plasmon absorption bands in the visible region. After reduction, the absorption spectra of the silver particles passivated by SCDPEU display strong absorption band at around 418 nm attributing to the



Scheme 1

surface plasmon absorption of silver colloids. Figure 1 provides spectroscopic evidence for Ag^+/Ag^0 loading into polydendron **1**. The symmetrical shapes of this plasmon band suggest that the reduced silver particles are well dispersed and sphere-shaped.

Antibacterial assessment

The design of antibacterial polymers is of continuing interest in biomaterials science for their effective applications as biomedical implants. In this context, silver doped materials exhibiting effective antibacterial properties [6, 9] have received considerable attention in recent years. The inert nature, non-toxicity and antimicrobial efficiency of silver make it an attractive

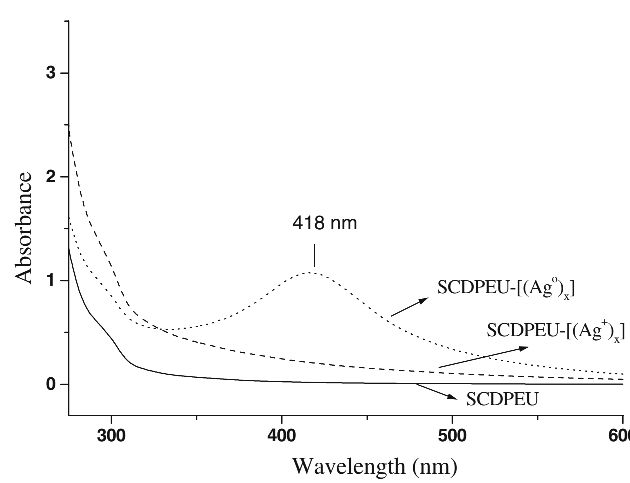


Fig. 1 UV-vis spectra of SCDPEU and its silver doped composites (SCDPEU-[$(Ag^+)_x$], SCDPEU-[$(Ag^0)_x$]

option for rendering polymeric biomaterials antimicrobial. In a recent study, we have observed the antibacterial activity of PAMAM dendron as well as its silver doped composites. Therefore, in this paper we have explored the anti bacterial activities of SCDPEU and SCDPEU-silver composites (SCDPEU-$[(Ag^+)_x]$, SCDPEU-$[(Ag^0)_x]$) against *Escherichia coli*.

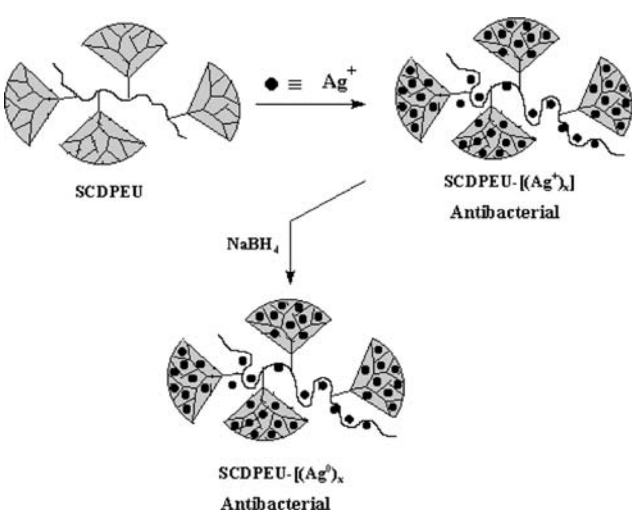
A control experiment was carried out with only DMSO: H_2O (1:1) to check the effect of its use during study. Moreover, a known antibiotic like amoxicillin (inhibition zone = ~20 mm) was also used for confirmation of the study of antibacterial activity against *E. coli* bacteria. From the data shown in Table 1, it was concluded that SCDPEU showed no inhibition zone.

However, the silver (Ag^+/Ag^0) doped polydendron inhibited the growth of the test bacteria on a solid agar medium after 18 h. These observations are in agreement with those reported in our previous paper. Regarding the oxidation states of silver, we observed no noticeable difference in the total area of zone of inhibition corresponding to the antibacterial behavior (Scheme 2).

Figure 2 shows the growth inhibitory effect of SCDPEU and its silver doped materials e.g, SCDPEU-$[(Ag^+)_x]$, SCDPEU-$[(Ag^0)_x]$. These results clearly demonstrate the antibacterial activity of both Ag^+ and Ag^0. This means that the introduction of metal ions, especially the silver ion or silver particle to SCDPEU develops its activity against *E. coli*.

Table 1 Diameters of Inhibition zones against *Escherichia coli* bacteria

Samples	Inhibition zones (mm)
SCDPEU	0
SCDPEU-$[(Ag^+)_x]$	10.5
SCDPEU-$[(Ag^0)_x]$	10.7



Scheme 2

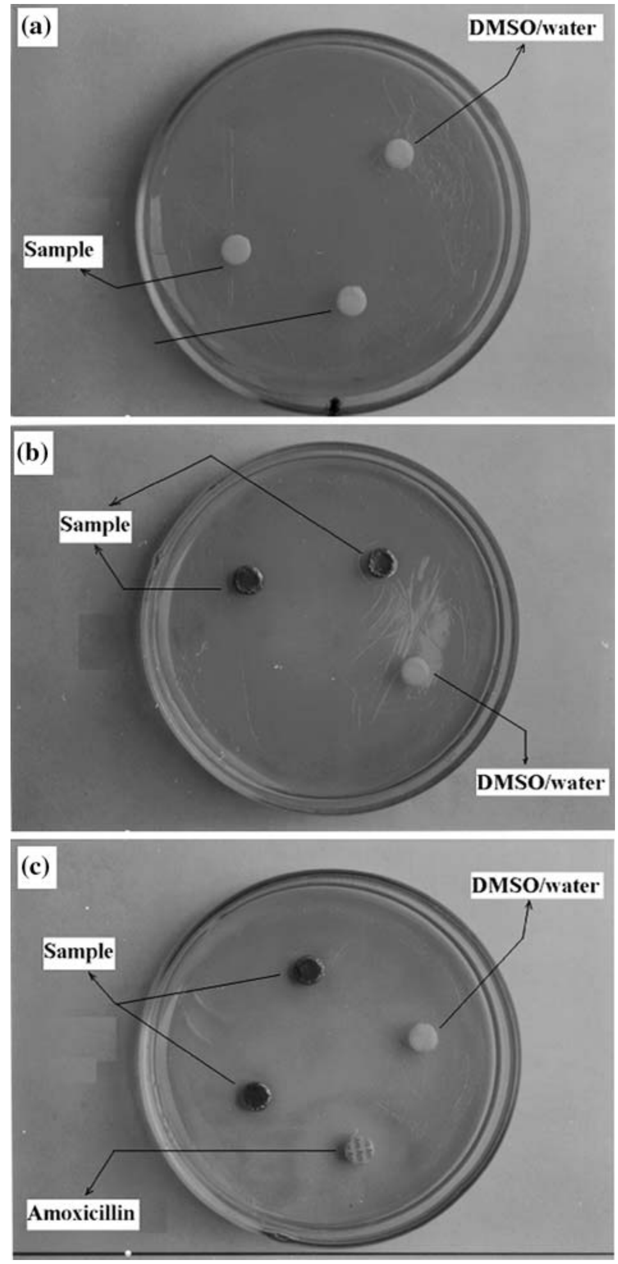


Fig. 2 Bacterial adherence to polymer samples kept in contact with *E. coli* bacteria (**a**) SCDPEU, (**b**) SCDPEU-$[(Ag^+)_x]$, (**c**) SCDPEU-$[(Ag^0)_x]$

Conclusion

Thus the primary evaluation of the antibacterial properties of SCDPEU and its silver based composites like SCDPEU-$[(Ag^+)_x]$, SCDPEU-$[(Ag^0)_x]$ has been achieved in vitro against *E. coli*. Silver doped materials only showed the antibacterial activity. Thus sequestering of SCDPEU with silver particles provides an important antibacterial polymeric attribute that will encourage its practical use for antimicrobial biomedical devices to meet the specific demand in hygienic living conditions and so forth. Further studies are under progress.

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