

Photoinitiated Crosslinking and Grafting of Methylmethacrylate Using N,N-Dimethyl Amino Functional Polystyrene Block Copolymers

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Monodisperse poly(*N,N*-dimethyl-4-vinylphenethylamine)-*block*-polystyrene was synthesized via anionic living polymerization carried out at -78 °C under a pressure of 10^{-6} torr using cumyl potassium as the initiator. Subsequent photoinduced radical polymerization of styrene through side chain-functional N,N-dimethyl amino groups yielded a crosslinked polymer and a brush type block-graft copolymer to a lesser extent. Upon irradiation at a wavelength of 350 nm, macroradicals were generated via hydrogen abstraction from amino side-chain groups by the excited benzophenone. The block-graft copolymer was characterized by ¹H-NMR, IR, and GPC analysis.

Key Words: Living anionic polymerization, photoinitiated radical polymerization, crosslinked polymer, brush block copolymer, block-graft copolymer.

Introduction

The synthesis of novel polymeric materials has recently become a widespread issue in polymer science. Block and graft copolymers that provide specific combinations of physical properties are the most suitable materials for various purposes¹. It appears that simple linear block copolymers may not be useful in the fabrication of polymeric devices exhibiting desirable sophisticated physical phenomena². Thus, polymer alloys consisting of block and graft copolymers might be useful.

Polymer brushes are an assembly of polymer chains attached to a surface at a high grafting density. When the brush regime is attained, the grafted chains begin to stretch away from the surface to avoid crowding. Because of the confinement and the uniform polymer constitution, the brush reacts collectively to environmental stimuli such as changes in the pH or ion strength, temperature, solvent quality, or mechanical forces³. These brush properties provide the basis for the fabrication of functional devices on a nanometer scale⁴.

There are several major techniques available for the preparation of grafted layers including physical adsorption of block copolymers⁵, attachment of end-functionalized polymers (“grafting onto” method)^{6–8},

and polymerization initiated from solid surfaces (“grafting from” method)^{9,10}. Block copolymer adsorption is a simple and reproducible technique. However, it results in a low grafting density and the immobilized polymers do not remain permanently on the surface. The “grafting onto” methods are self-limiting because the grafted chains hinder the approach of additional polymer chains to the surface. The polymer brushes obtained by the “grafting from” technique, in which self-assembled monolayers of initiators are used to grow chains outward from the surface, possess the extremely high density of the attached chains^{3,4,11}.

Polymeric photoinitiators are precursors for block or graft copolymers depending on the position of the photoinitiator moiety incorporated into the polymer chain. In a previous study, we prepared a block copolymer from a precursor *N,N*-dimethyl aniline end-functional polystyrene synthesized by atom transfer radical polymerization¹². Upon irradiation in the presence of a sensitizer, a macroradical, which was formed via hydrogen abstraction by the excited sensitizer, initiated radical polymerization of methylmethacrylate or was further oxidized to initiate cationic polymerization of cyclohexene oxide.

In this study, we report the preparation of methylmethacrylate brushes on a diblock copolymer backbone using a photoinduced “grafting from” strategy. The AB-type precursor block copolymer was synthesized through living anionic polymerization, in which the ‘A’ segment contained no functional groups whereas the ‘B’ segment held *N,N*-dimethyl amino groups in each repeating unit. Subsequently, block-graft brushes (2) were prepared by photoinitiated radical polymerization of methylmethacrylate from corresponding *N,N*-dimethyl amino groups. Concomitant formation of crosslinked polymers was also observed.

Experimental

Materials

N,N-Dimethyl-4-vinylphenethylamine (PTA), cumyl potassium, styrene (St) and THF were purified according to the conventional method for anionic living polymerization¹³. Benzophenone (Fluka) was used as received. Methyl methacrylate (Aldrich) was purified by the conventional method and distilled at reduced pressure over calcium hydride (CaH₂) before use. 4-Hydroxy-2,2,6,6-tetramethyl-1-piperidinyl-1-oxy (HTEMPO) (Aldrich) was used without further purification.

Preparation of poly(*N,N*-dimethyl-4-vinylphenethylamine)-block-polystyrene

N,N-Dimethyl-4-vinylphenethylamine (PTA) and cumyl potassium were prepared according to a previously described method. Preparation of the diblock copolymer was performed by sequential addition of the PTA and St to the polymerization solution. Polymerization was performed in a sealed glass apparatus at -78 °C in THF under a pressure of 10⁻⁶ torr, following essentially the same procedures as described in previous studies¹³⁻¹⁶.

General procedure for photopolymerization reactions

Monomer (MMA) either in bulk form or in solution with dichloromethane, sensitizer (benzophenone), and macroinitiator (poly(*N,N*-dimethyl-4-vinylphenethylamine)-*block*-polystyrene) were put into a Pyrex tube; degassed with nitrogen; and irradiated at room temperature in a merry-go-round type photoreactor equipped with 15 Philips lamps and emitting light nominally at 350 nm. At the end of irradiation, the content of the tube was dissolved in dichloromethane, and filtered, while the undissolved portion was collected separately.

The soluble polymer was precipitated in 10-fold excess methanol. Finally, the solid polymer was collected by filtration and dried overnight at reduced pressure.

Photosensitized side chain HTEMPO capping of poly(*N,N*-dimethyl-4-vinylphenethylamine)-*block*-polystyrene

Into a Pyrex tube containing 40 mL of dichloromethane were added 0.30 g (1.9×10^{-4} mol/L) of poly(*N,N*-dimethyl-4-vinylphenethylamine)-*block*-polystyrene, 0.22 g (3×10^{-2} mol/L) of benzophenone and 0.30 g (4.3×10^{-2} mol/L) of HTEMPO. The solution was degassed and the tube was sealed under nitrogen prior to irradiation in the photoreactor. Cupric sulfate aqueous solution was used as the photofilter in order to avoid the absorption of HTEMPO. After 24 of irradiation at 25 °C, the polymer was precipitated in methanol, filtered and dried overnight at reduced pressure.

Characterization

GPC analyses of the polymers were performed at room temperature using a Waters instrument equipped with an R410 differential refractometer and 600E pump. THF with a flow rate of 1.0 mL/min was used as the eluent. Molecular weights were calculated on the basis of a calibration curve recorded with monodisperse polystyrene standards. ¹H-NMR measurements were carried out in CDCl₃ solution using a Bruker 250 MHz instrument. The IR spectra were recorded on a Shimadzu IR-470 infrared spectrophotometer.

Results and Discussion

Poly(*N,N*-dimethyl-4-vinylphenethylamine-*block*-styrene), [P(PTA-*b*-St)] block copolymer was synthesized by sequential addition of *N,N*-dimethyl-4-vinylphenethylamine (PTA) and styrene (St) by anionic living polymerization as described previously^{13–16}. The experimental conditions and results are presented in Table 1.

Table 1. Experimental conditions and results for the preparation^a of poly(*N,N*-dimethyl-4-vinylphenethylamine)-*block*-polystyrene, PDPTA-*b*-PSt diblock copolymer.

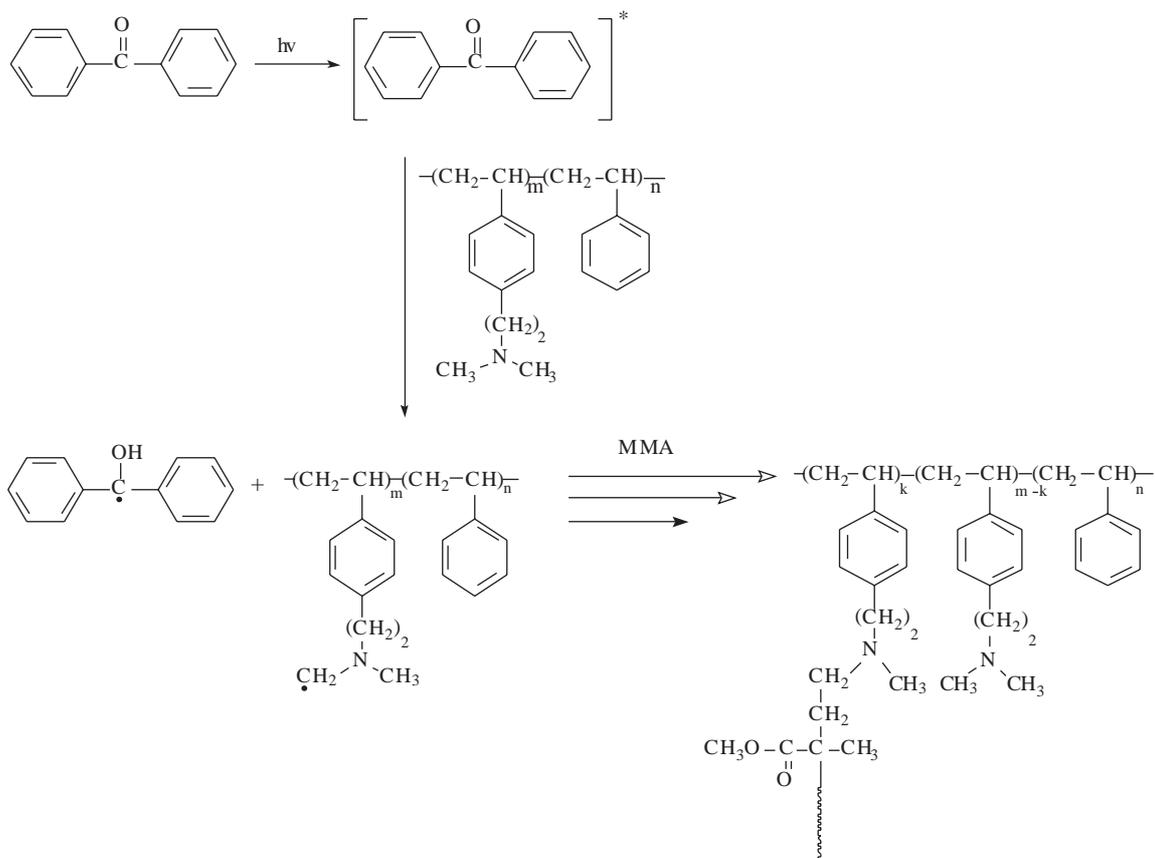
DPTA (g)	Time (h)	St (g)	Time (h)	Solvent ^b (mL)	Initiator ^c (mmol)	Conv. (%)	PSt content (%)	Mn ($\times 10^{-4}$)	M _w /M _n ^d
3.4	10	3.9	3.5	160	0.15	100	53	2.2	1.01

^a Polymerization was carried out at -78 °C under a pressure of 10^{-6} torr,

^b THF, ^c cumyl K,

^d Determined from GPC measurement.

The diblock copolymer containing *N,N*-dimethyl amino groups in one segment was used as a backbone to explore the possibility of using photoinduced radical polymerization in the preparation of polymer brushes by the a “grafting from” method. As depicted below (reactions 1-3), the mechanism involves hydrogen abstraction by the photoexcited benzophenone from *N,N*-dimethyl amino groups. The carbon centered radicals thus generated are able to initiate the free radical polymerization of methylmethacrylate (MMA)¹².



The formation of block-graft copolymer was evidenced by GPC and $^1\text{H-NMR}$ analyses. Shifting of the initial unimodal GPC peak of precursor diblock copolymer to higher elution volumes indicates that grafting was successfully established (Figure 1). Furthermore, as seen in the $^1\text{H-NMR}$ spectrum of the polymer recorded after photopolymerization, the peak appearing at about 3.6 ppm corresponding to O-CH₃ protons shows the presence of grafted MMA units in the final polymer (Figure 2). The results are summarized in Table 2. It is interesting to note the effect of both initiator concentration and irradiation time on the conversion and molecular weights.

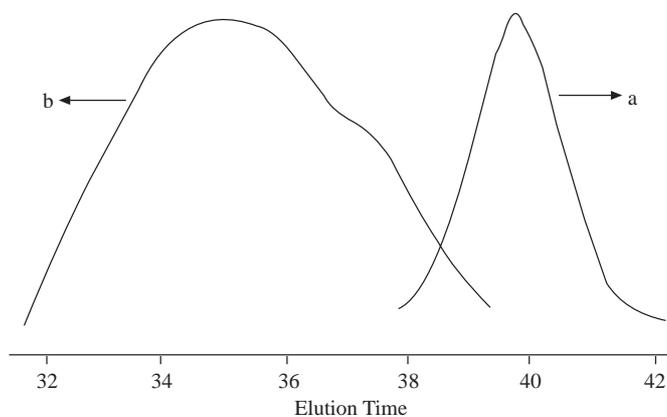


Figure 1. GPC traces of precursor [P(PTA-*b*-St)] block copolymer (a), and final block- graft copolymer (b).

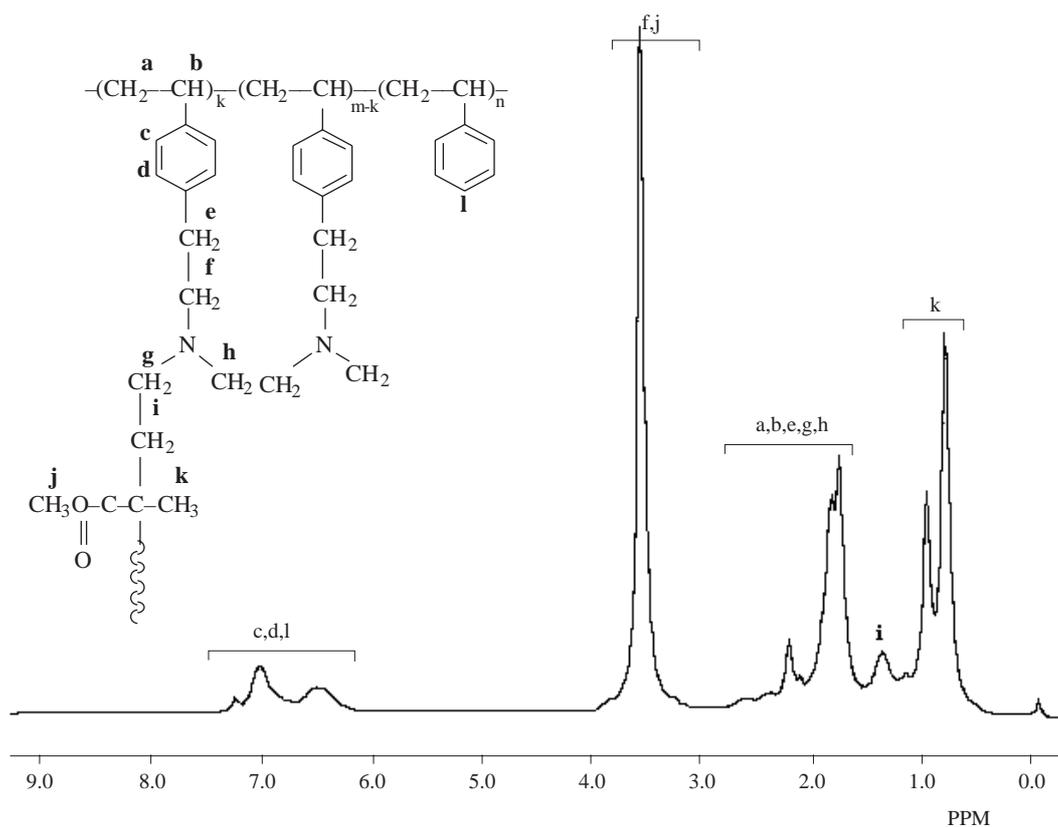


Figure 2. $^1\text{H-NMR}$ spectrum of [poly((*N,N*-dimethyl-4-vinylphenethylamine)-*graft*-polymethylmethacrylate)]-*block*-polystyrene.

Table 2. Preparation of [poly((*N,N*-dimethyl-4-vinylphenethylamine)-*graft*-polymethylmethacrylate)]-*block*-polystyrene, (PDPTA-*g*-PMMA)-*b*-PSt block-graft copolymer via photoinduced radical polymerization^a of MMA.

Run	[M] (mol/L)	[I] ^d (g/L)	Irrad.time (min)	Conversion (%)	$M_n^{e,f}$	$M_w/M_n^{e,f}$
1 ^b	9.43	10	30	9.0	75,300	2.67
2 ^c	4.72	10	30	6.8	30,600	1.29
3 ^c	4.72	5	30	18	51,700	2.70
4 ^c	4.72	10	10	4.9	41,850	2.77

^a $\lambda_{inc.}$ = 350 nm, ^bbulk, ^csolution,

^d poly(*N,N*-dimethyl-4-vinylphenethylamine)-*block*-polystyrene,

^esoluble polymer,

^fDetermined from GPC measurement.

In the experiments, formation of crosslinked polymer was observed to a greater extent. In all cases, crosslinking yield was 80% or more. The crosslinking mechanism may be explained by the participation of unsaturated chain ends, formed by the disproportionation reaction, in a further radical attack. The presence of absorption bands belonging to methylmethacrylate appearing at about 1735 cm^{-1} (C=O stretching) and 1150 cm^{-1} (C–O stretching) in the IR spectrum of crosslinked polymer (Figure 3) supports that monomer was involved in crosslinking. Moreover, the possibility of macroradical attack by other growing species in the

chain termination may be another reason for the crosslinking reactions as methylmethacrylate polymerization is known to be terminated partly by chain combination besides disproportionation. This possibility was further investigated by experiments carried out in the absence of monomer. A control experiment produced an insoluble polymer network after 30 min of irradiation under identical conditions except for the fact that no monomer was available in the reaction medium. This suggests that a combination of backbone copolymers through the carbon centered radicals stemming from the *N,N*-dimethyl amino side groups may also contribute to crosslinking.

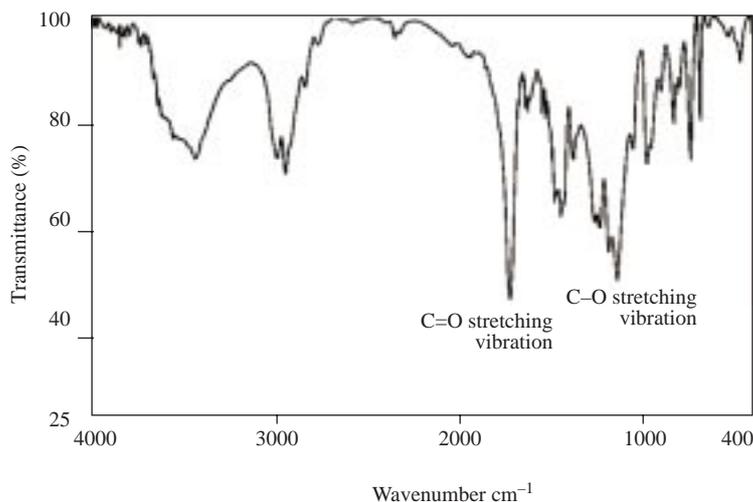
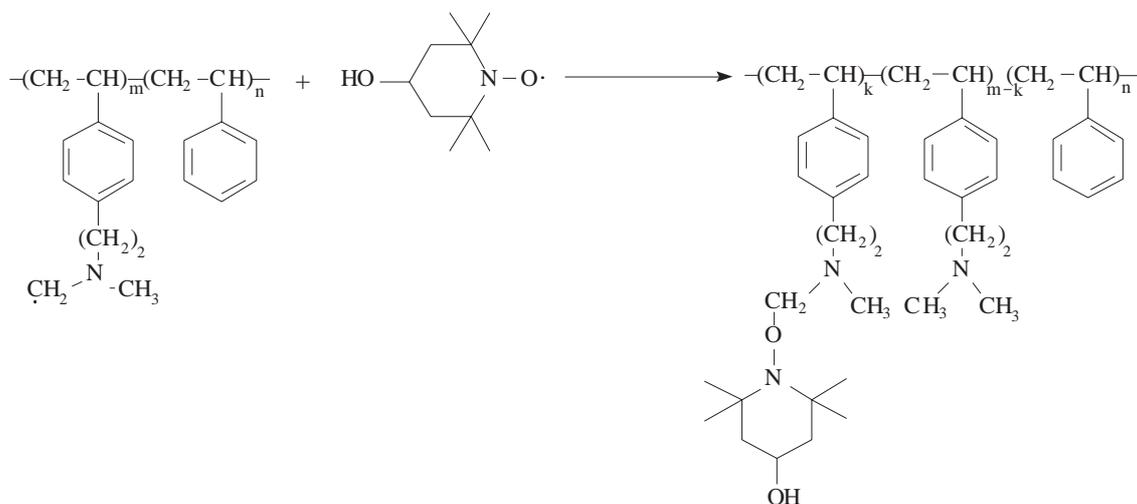


Figure 3. IR spectrum of the crosslinked polymer on KBr disk.

In order to gain a greater insight into the grafting mechanism, photochemically generated radicals, formed according to reaction 2, were reacted with the stable radical, 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyl-1-oxy (HTEMPO), in the absence of the monomer as illustrated in reaction 4. Figure 4 gives the ¹H-NMR spectra of poly(*N,N*-dimethyl-4-vinylphenethylamine)-*block*-polystyrene (A) before and (B) after capping with HTEMPO. The new proton signals appearing at 1.09 and 1.17- (-CH₃), 3.73 (-CH-), and 5.29 (-CH₂-) proved that HTEMPO moieties were incorporated into the polymer. This implies that upon irradiation, grafting takes place through the radicals formed on the side chains.



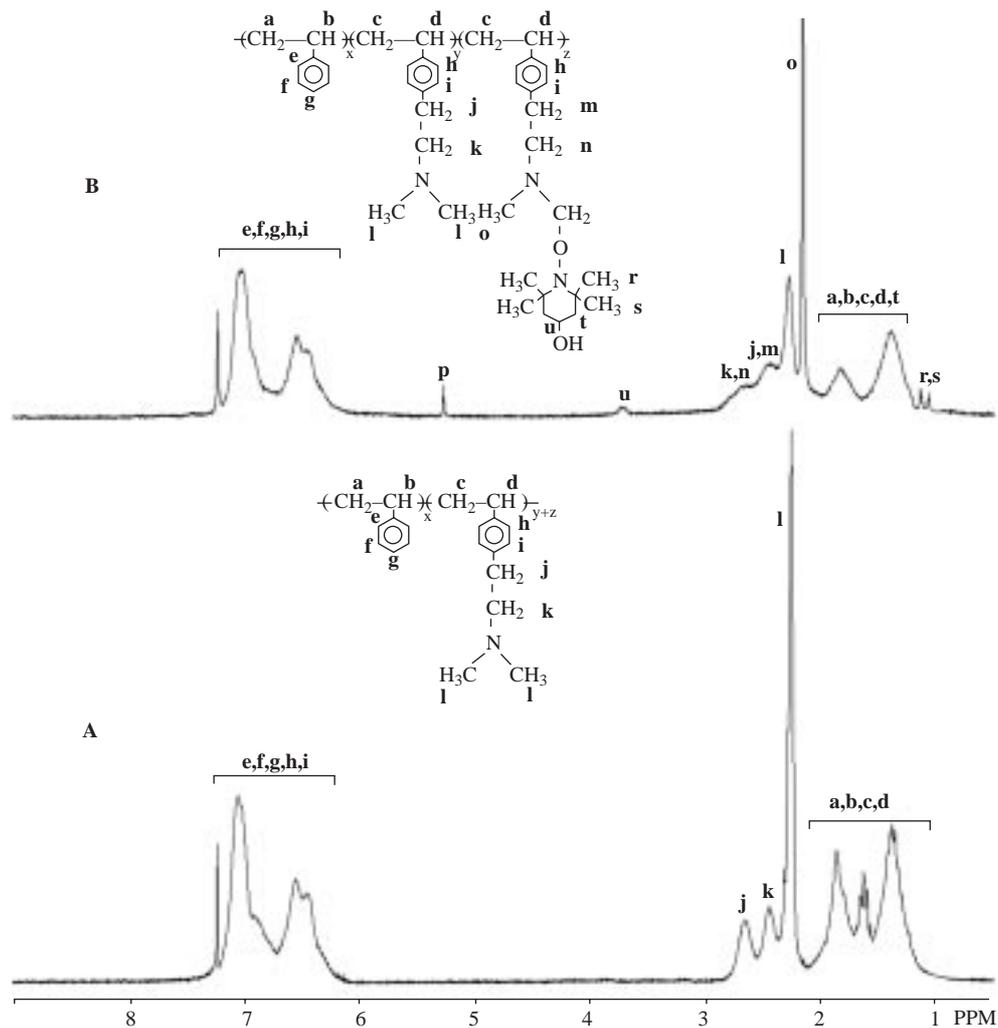


Figure 4. $^1\text{H-NMR}$ spectra of poly(*N,N*-dimethyl-4-vinylphenethylamine)-*block*-polystyrene before (A) and after capping with HTEMPO (B).

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