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Synthesis of Amphiphilic Polystyrene–Ionene Diblock Copolymers with Controlled Block Lengths

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Abstract: Amphiphilic polystyrene–ionene diblock copolymers with blocks of controlled molecular weights were synthesized by a new method. The preparation starts with the anionic polymerization of styrene with 3-(dimethylamino)propyllithium as initiator, yielding tertiary amino end-functionalized polystyrenes of molecular weights that can be varied over a wide range from 1 to 100 kg/mol, and a relatively low polydispersity ($\bar{M}_w/\bar{M}_n = 1.1\text{--}1.4$). The crucial step in this method is the stepwise coupling of the reactive end-group of the polystyrene with bromo- and tertiary-amino-terminated monodisperse oligomeric 2,4-ionenes. The amphiphilic polymers with well-defined block lengths were characterized by thin-layer chromatography, end-group titration and elemental analysis. Amphiphilic block copolymers with a monodisperse ionene block consisting of up to 10 quaternary ammonium groups could be derived.

Key words: (di)block copolymer, anionic polymerization, dimethylamino functionalized polystyrene, 3-(dimethylamino)propyllithium, poly(quaternary ammonium salt), 2,4-ionene.

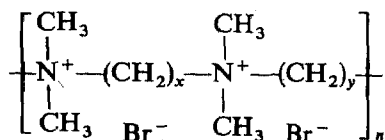
INTRODUCTION

Modified copolymers containing quaternary ammonium groups or ionene block segments exhibit unique properties and various interesting applications. For example, incorporating quaternary ammonium groups in elastomeric materials often results in thermoplastic behaviour.¹ Also, elastomeric ionenes of the polyurethane type^{2,3} and block copolymer ionenes with polytetrahydrofuran sequences^{4,5} have been reported. Furthermore, to obtain conducting elastomers Ikeno *et al.*⁶ synthesized ionene polymers containing poly(tetramethylene oxide) chain units, which, after addition of a doped salt to the ionene, exhibited electrical properties.

Apart from improvement of mechanical or electrical properties, polymers containing quaternary ammonium groups also exhibit strong promoting effects in certain

catalytic reactions.⁷ The addition of ionenes (Fig. 1) leads to a 50-fold rate enhancement for the oxidation of thiols catalysed by cobalt(II)phthalocyanine-tetra(sodium sulphonate) ($\text{CoPc}(\text{NaSO}_3)_4$). The increase results in part from the formation of the polymer-stabilized dimeric or aggregated structure of the catalyst.⁸ Besides stimulation of the aggregated form, the ionene induces substrate enrichment at the catalytic site and also prevents formation of an inactive μ -peroxo-complex of the catalyst. Altogether, these factors lead to a highly efficient catalytic system. It has also been demonstrated that diblock copolymers consisting of an ionene sequence and either a polystyrene block⁹ or an alkyl chain¹⁰ show further enhancement of the catalytic activity in the autoxidation of hydrophobic thiols as compared with the homopolymer of 2,4-ionene. The copolymer containing a polystyrene block proved to be the most effective promoter, as a result of a stronger hydrophobic interaction with the hydrophobic thiol. Hence, it can be concluded that

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Fig. 1. x,y -Ionene.

an ionene sequence extended with a polystyrene block is the best promoter for the $\text{CoPc}(\text{NaSO}_3)_4$ -catalysed oxidation of hydrophobic thiols. The present paper deals with the synthesis of well-defined block copolymers, which is a prerequisite for the optimization of the above oxidation reactions.

It has been shown before that, because of the completely different mechanisms of ionene and polystyrene polymerization, the only route to such a polystyrene-ionene diblock copolymer is by reactive end-coupling.⁹ The best route towards reactive end-group functionalized polystyrene is the anionic polymerization of styrene, starting with a functional initiator. For example, if the initiator is equipped with a tertiary amino group, in a second step the resulting amino end-functionalized polystyrene will be able to react with the bromo end-groups of an ionene oligomer. By introducing the amino group in the initiation step, incomplete functionalization will be circumvented. A functional initiator that is very suitable for this type of functionalization is 3-(dimethylamino)propyllithium (DMAP-Li), first introduced by Eisenbach and co-workers.^{11,12} More recently, DMAP-Li has been applied to prepare tertiary amino terminated polyisoprene,¹³ polybutadiene¹⁴ and polystyrene.¹⁵

In this paper we present the coupling of functionalized polystyrene with ionene, and the difficulties arising during the preparation will be discussed. Furthermore, it will be demonstrated that the new method of extending the polystyrene block with ionene can even be applied to relatively high molecular weight polystyrenes, and it will be shown that, in principle, the monodisperse ionene blocks can be prepared at any desired chain length. This will allow the preparation of amphiphilic polystyrene-ionene diblock copolymers with a wide range of controlled block lengths. These tailor-made block copolymers then can be used and optimized as promoters of the oxidation of hydrophobic thiols, resulting in extremely efficient catalytic systems.

EXPERIMENTAL

Preparation of dimethylamino functionalized polystyrene

The synthesis of 3-(dimethylamino)propyllithium was carried out in *n*-hexane, by a reaction of 3-(dimethylamino)propylchloride with an excess of lithium, keeping the temperature below 20°C to minimize Wurtz coupling. After purification, the initiator was stored in benzene at -15°C before use.¹⁴ Styrene, initiated by DMAP-Li, was

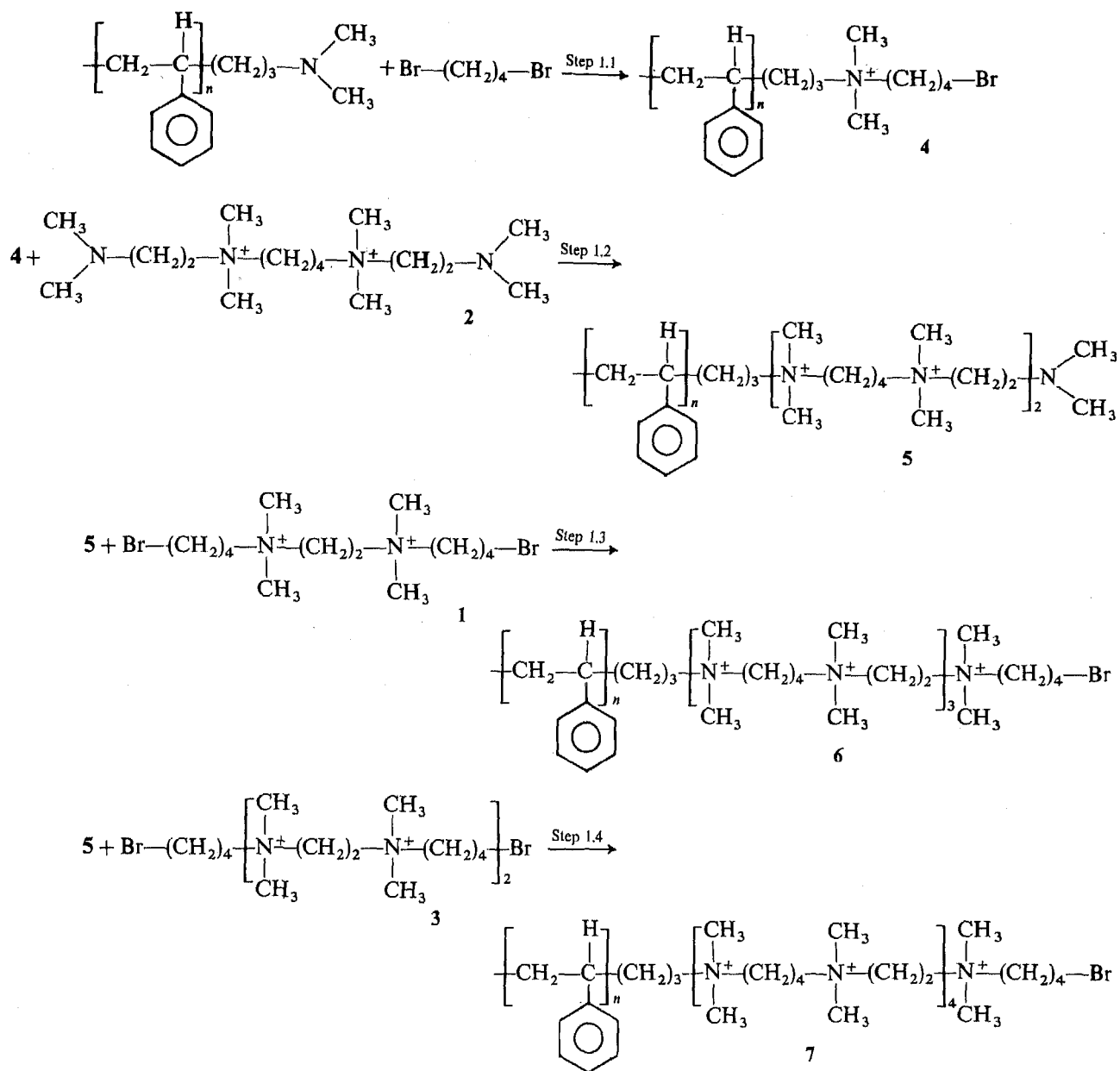
polymerized anionically in a mixture of toluene and tetrahydrofuran at 40°C.⁹

Synthesis of monodisperse oligomers of 2,4-ionene

The oligomers of 2,4-ionene were all prepared according to procedures previously reported.⁹ The Br-terminated trimer of 2,4-ionene (1) was prepared by reacting a large (20-fold) excess of 1,4-dibromobutane with *N,N,N',N'*-tetramethylethylenediamine (TMEDA) in a CH_3OH -DMF mixture. Subsequently, the *N*-terminated trimer of 2,4-ionene (2) was synthesized by reacting an excess of TMEDA with 1,4-dibromobutane. To obtain the Br-terminated pentamer (3), the *N*-terminated trimer (2) was reacted with a large amount of 1,4-dibromobutane in a mixture of DMF, CH_3OH and water. The bromo-terminated 2,4-ionene polymer ($\bar{M}_n = 1.65 \text{ kg/mol}$) was prepared according to the method described by Rembaum *et al.*¹⁶ The molecular weights of all the products could easily be determined by titration of the tertiary amino end-groups of the ionene oligomers with HCl. For that purpose, it was necessary to end-cap the Br-trimer (1), Br-pentamer (3) and Br-terminated 2,4-ionene polymer with an amino moiety, by reacting with an excess of TMEDA. The molecular weights of the oligomers obtained were in close agreement with their theoretical values.

Reactive end-coupling of dimethylamino functionalized polystyrene with ionene oligomers

The coupling of low molecular weight polystyrene ($\bar{M}_n < 3 \text{ kg/mol}$) with small oligomeric units of 2,4-ionene was performed according to procedures described earlier.⁹ A typical procedure for coupling relatively high molecular weight polystyrene started with reacting the polystyrene ($\bar{M}_n = 12.6 \text{ kg/mol}$) with a 60-fold excess of 1,4-dibromobutane in DMF for 1 day at 50°C (Scheme 1, Step 1.1). Then, the polymer (4) was precipitated in 2-propanol and dried under vacuum. The second step was the coupling of the quaternized polystyrene (4) (5.2 g dissolved in 31 ml of DMF) with a 30-fold excess of *N*-terminated trimer (2) (5.6 g in 7 ml of CH_3OH and 12 ml of DMF) (Step 1.2). When mixing both solutions an extra 12 ml of DMF had to be added to obtain a clear solution. The reaction was complete after 2 days at 50°C, and was followed by a purification procedure that comprised precipitation of the block copolymer in water, and, after filtering, washing with water and drying under vacuum. The next step was to dissolve 5.0 g of the resulting polymer (5) in 31 ml of DMF, and then add a mixture of a 25-fold excess of Br-trimer (1) (5.1 g) in 10 ml of CH_3OH , 2.5 ml of H_2O and 9 ml of DMF (Step 1.3). An additional 40 ml of DMF was added to avoid any possible precipitation. After 7 days at 50°C the block copolymer (6) was purified according to the above procedure. Further extension of the ionene block has been performed with 2 g of the



Scheme 1. Various routes of coupling polystyrene with monodisperse oligomers of 2,4-ionene.

polymer (6) and a 20-fold excess of *N*-trimer (2) in 3 ml of CH₃OH and 24 ml of DMF for 14 days at 50°C, followed by the above purification method. This resulted in an ionene block of 10 quaternary ammonium groups.

Characterization

Analysis by size exclusion chromatography (SEC) was performed at a flow rate of 1 ml/min in tetrahydrofuran at 40°C using a Waters high-performance liquid chromatography (HPLC) system (UV detector), equipped with two linear Shodex columns. The number average molecular weights of both the polystyrenes, and of the diblock copolymers, were determined by titration of the dimethylamino chain end in a 1:1 (v/v) mixture of glacial

acetic acid and chloroform (both Merck p.a.), with perchloric acid (0.0995N in acetic acid, Aldrich) as titrant and Methyl Violet as indicator.¹⁷ Thin-layer chromatography (TLC) was performed on SiO₂ plates (Merck Art. 5554), using a mixture of chloroform and methanol (9:1, v/v) as eluent.¹⁸

RESULTS AND DISCUSSION

As can be seen in Table 1, styrene can be polymerized to any desired degree of polymerization by an anionic technique using the functional initiator 3-(dimethylamino)propyllithium. The initiator is suitable for the preparation of polystyrenes of a broad range of molecular weights varying from 1 to 100 kg/mol. The molecular

TABLE 1. Molecular weights of the polystyrenes prepared with 3-(dimethylamino)propyllithium

Polystyrene	End-group titration \bar{M}_n (kg/mol)	Size exclusion chromatography	
		\bar{M}_n (kg/mol)	\bar{M}_w/\bar{M}_n
A	1.1	1.2	1.3
B ^a	2.7	2.1	1.4
C ^a	5.2	2.6	1.3
D	7.8	11.2	1.1
E	8.4	12.6	1.4
F ^a	9.2	9.3	1.4
G	17	12	1.2
H	43	35	1.1
I	50	36	1.2
J	84	82	1.1

^a Ref. 9.

weight distributions of the products of the anionic polymerizations are not as small as those for an *n*-butyllithium-initiated polymerization, as a result of the less nucleophilic character of the functional initiator used here.

All polystyrenes obtained showed characteristics with respect to the molecular weight distributions similar to those found by Ikker,¹⁵ who prepared DMAP-Li sonochemically and performed the polymerization under high-vacuum conditions. Ikker also showed that variation of the amount of THF added during the anionic polymerization had no influence on the dispersity.

In addition, in Table 1 it can be seen that no large discrepancies are found between the molecular weights determined by end-group titration and by SEC. All chromatograms were typical of narrow-distribution polystyrenes, indicating that the functional groups of the polystyrenes did not lead to polymer adsorption onto the column.

Before extending the polystyrene obtained with an ionene chain, one has to realize that a direct coupling between the reactive end-groups of polystyrene and a 2,4-ionene polymer is not straightforward, because of the large differences in solubility.¹⁹ Polystyrene dissolves only in very low concentrations in a solvent for ionene and vice versa. As a first attempt, we tried to couple polystyrene with Br-terminated 2,4-ionene in a CHCl₃-CH₃OH mixture, in which both polymers dissolve, but this approach raised a problem: the concentrations of the reactive end-groups were so low that even after a long reaction period no conversion could be detected. Therefore, the only route to couple both polymers seemed to be to react high concentrations of small units of 2,4-ionene with the polystyrene. Of course, the polystyrene can be extended by reacting with 1,4-dibromobutane and TMEDA, the two monomers of 2,4-ionene, successively, but this is inconvenient because of the many reaction steps involved.

The new concept we developed starts with the quaternization of the polystyrene with 1,4-dibromobutane (Scheme 1, Step 1.1), followed by reaction with the *N*-terminated trimer (2) (Step 1.2). The most important reason for choosing this method, rather than reacting the polystyrene first with the Br-trimer (1), is that the *N*-trimer (2) dissolves to much higher concentrations (17 mM) in an appropriate quaternization solvent such as DMF than does the Br-trimer (1) (2 mM). Besides variations in the molecular weight, the differences in the hydrophilicity of the end-groups and the fact that the distance between the two ammonium groups in the *N*-trimer (2) is larger than in the Br-trimer (1) determine the discrepancy in solubility. Consequently, a better solubility of the reactants results in a higher concentration of reactive end-groups, which is an important factor in these coupling reactions. Another advantage of this procedure is that the reactive bromo end-group will be more accessible for further coupling. This is important because the chemical modification of linear polymers is usually more difficult than that of their low molecular weight analogues. For example, during the hydrolysis of poly(chloromethylstyrene), the macromolecule is present in solution in a tightly coiled conformation, such that the polymeric environment almost forms a separate phase, which implies that no hydrolysis can take place, in contrast with its monomeric analogue.²⁰ Similar effects may be operative in the present case, where the chain end is still too hydrophobic to react with ionene.

The conversion of these coupling reactions can easily be followed by TLC, because of the strong adsorption of aminated and quaternized polystyrene on silica. Polystyrene ($\bar{M}_n < 10$ kg/mol) extended with one or more quaternary ammonium group can easily be separated from the non-quaternized polystyrene by TLC. However, no difference in *R_f* value was found between non-quaternized and quaternized polystyrenes of molecular weights exceeding 10 kg/mol.

TABLE 2. Data characterizing the amphiphilic polystyrene-ionene diblock copolymers

Polystyrene block	No. of quaternary ammonium groups of ionene block	Nitrogen content (theoretical)	Nitrogen content (experimental)	End-group	\bar{M}_n (titration) (kg/mol)
B	4	2.08	1.65	N	1.6
B	9	2.94	1.99	Br	^a
C	4	2.08	1.95	N	6.2
C	9	2.94	2.27	Br	—
E	4	0.53	—	N	6.5
E	7	0.71	0.70	Br	^a
E	10	1.08	0.78	N	60
F	4	0.71	0.57	N	10.7
F	7	0.94	0.96	Br	^a

^a Direct change of colour in the titration, indicating a bromo end-group.

TLC showed complete conversion for both Steps 1.1 and 1.2 within a reasonable reaction time of 1 or 2 days. Also, the nitrogen content as determined by elemental analysis (Table 2) confirmed the formation of polystyrenes extended with four quaternary ammonium groups. Supporting evidence for the completeness of the coupling reactions was derived from titration of the tertiary-amino-terminated amphiphilic polymers with perchloric acid, which showed molecular weights comparable with the theoretical values.

Further extension of the polymers proceeded as indicated in Scheme 1. Polystyrenes E and F (see Table 1) could be coupled further with a Br-trimer (1) (Step 1.3) and polystyrenes B and C with a Br-pentamer (3) (Step 1.4). At this point, TLC became useless in determining conversions, so other characterization techniques had to be used. To elucidate the success of the coupling, first elemental analysis was utilized. As can be seen in Table 2, the experimental values were somewhat lower than the corresponding theoretical values, indicating that incomplete conversion had taken place. Unfortunately, the experimental values showed large deviations. Similar problems have been encountered before in the elemental analysis of ionenes.²¹ The discrepancies we observed could result from the tendency of ionenes to absorb water, especially when bromine is the counterion.²² This highly hygroscopic behaviour should be reflected in a higher hydrogen content, which indeed was detected in some cases. Nevertheless, despite the low accuracy of elemental analysis, the increasing nitrogen content proved that a high degree of conversion was reached after coupling with the Br-terminated oligomers. In addition, the resulting amphiphilic polymers were titrated with perchloric acid, to confirm the absence of amino end-groups. These titration experiments showed clearly the absence of amino groups, indicating very high conversions. The strongest arguments confirming the high conversions in the coupling reactions were derived from previously

described coupling experiments between Br-trimer (1) or Br-pentamer (3) with polystyrene, which unambiguously showed that the reaction was completed within an acceptable reaction time.⁹ Therefore, it can be concluded that Steps 1.3 and 1.4 can be performed to high conversions.

Because of the excellent solubility of the *N*-trimer (2) in DMF, the polystyrene E obtained can be even further extended, resulting in 10 quaternary ammonium groups. Titration, followed by elemental analysis, confirmed the formation of this type of polystyrene-ionene block copolymer.

As our final goal is the use of the amphiphilic polymer as a promoter in the CoPc(NaSO₃)₄-catalysed autoxidation of hydrophobic thiols, it is not necessary to obtain polystyrene-ionene block copolymers with high ionene block lengths. Monodisperse 2,4-ionene with four or six quaternary ammonium groups already perfectly stabilizes the aggregated form of CoPc(NaSO₃)₄, and hence exhibits excellent promoting activities in the CoPc(NaSO₃)₄-catalysed oxidation of hydrophobic thiols.²³

To optimize and improve this novel method, we examined the influence of the molecular weight of the polystyrene segments on the extension reaction, eventually leading to the determination of the most important parameters for the coupling reactions. The influence of the length of the polystyrene segments was studied by performing the extension reaction of Br-trimer (1) with two different polystyrenes ($\bar{M}_n = 43$ kg/mol and 84 kg/mol). No conversion could be detected after the coupling of the longest polystyrene and only very low conversions were observed for the smaller one. Thus, if the molecular weight of the polystyrene exceeds 20 kg/mol, coupling with Br-trimer (1) becomes very difficult, as a result of its lower solubility in DMF.

As already shown earlier, we succeeded in a direct coupling of a Br-pentamer (3) ($\bar{M}_n = 0.88$ kg/mol) with polystyrene.⁹ Now the question arises if it is possible to

combine polystyrene C ($\bar{M}_n = 2.6$ kg/mol) with an even higher, but still relatively low molecular weight Br-terminated 2,4-ionene ($\bar{M}_n = 1.65$ kg/mol), within a reasonable reaction period under the same conditions, as this would reduce the number of reaction steps in preparing this type of amphiphilic block copolymer. After a reaction time of 30 days a conversion of less than 10% was detected, which has to be attributed to the low concentrations of reactive end-groups. Hence, it can be concluded that the most important parameters in the present synthesis are the solubilities of the polymers and the concentrations of the reactive end-groups in a suitable quaternization solvent.

We have shown that it is possible to couple polystyrene, even when it has a relatively high molecular weight, with ionene of controlled block length. The effects of these amphiphilic diblock copolymers on the catalytic autoxidation of hydrophobic thiols in various solvents is now being investigated. One of our goals in the near future is to apply amphiphilic polystyrene-diblock copolymers as a surfactant during emulsion polymerizations, to obtain well-defined latices with ionene chains at the particle surface. This approach would enable us to perform the CoPc(NaSO₃)₄-catalysed oxidation of hydrophobic as well as hydrophilic thiols heterogeneously.

CONCLUSIONS

3-(Dimethylamino)-propyllithium proves to be a good initiator in preparing amino end-functionalized polystyrenes of low dispersities over a wide range of molecular weights. Reactive end-coupling with ionene appears to be dependent on the solubilities of the reactants and the concentrations of the reactive groups. According to the present method, polystyrenes with relatively high molecular weights (up to about 20 kg/mol) can be extended with an ionene block. Furthermore, TLC and end-group titration of the block copolymers appear to be good characterization techniques for this block copolymer synthesis route. Amphiphilic polystyrene-ionene diblock

copolymers can be prepared with a monodisperse ionene block containing between one and 10 quaternary ammonium groups.

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