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Controlled/“Living” Radical Polymerization with Dendrimers Containing Stable Radicals

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ABSTRACT: TEMPO-based stable radicals were attached to dendrimers of variable size and used to control radical polymerization of styrene, vinyl acetate, and (meth)acrylates. Thermal polymerization of styrene with [G-2]-TEMPO proceeded in a similar but not better controlled manner than with TEMPO alone. In the polymerization of styrene initiated with BPO, the kinetics and the molecular weight/conversion relations showed the same tendency as with TEMPO, though the polydispersity was higher than in the absence of dendrimers. This indicates that homolytic cleavage occurs at the reaction temperature, monomer can diffuse inside the cavity of the dendrimer, and polymer is at least partially compatible with the dendrimer. Model reactions indicate that the higher observed polydispersities could not be ascribed to transfer to benzyl hydrogen atoms. Therefore, the higher polydispersities could originate from the self-initiated polymerization of styrene outside of the dendrimers as well as the slow exchange of these chains with chains attached to dendrimers. To evaluate the effect of self-initiation, vinyl acetate, methyl methacrylate, and *n*-butyl acrylate were used; however, the resulting polymers were incompatibile with the dendrimers. The growing chains are easily released from the cavity of the dendrimers into solution, and their return into the cavities of the dendrimers was not fast enough to control the polymerization. The results of the polymerization in decalin solution indicate that polymerization of these monomers is better controlled but only at the early stages of the polymerizations. The subsequent precipitation of polymers attached to the dendrimers prevents further polymerization. These results suggest that the main reason for the higher observed polydispersities is not termination between growing chains but either decomposition of alkoxyamines or self-initiation occurring simultaneously with the slow propagation.

The preparation of well-defined polymers requires living systems in which the contribution of chain-breaking reactions such as transfer and termination can be neglected. Much interest has been recently focused on the preparation of well-defined polymers by the radical mechanism due to the facile reaction conditions as well as the large number of monomers which can be polymerized and copolymerized radically. The main obstacle in the synthesis of well-defined polymers by radical processes is the unavoidable bimolecular termination between growing radicals. However, the contribution of termination decreases with the reduction of radical concentration because termination is the second-order process with respect to growing radicals whereas propagation is first order in radicals. If a very low concentration of growing radicals is used in a conventional radical process, either dead-end polymerization or uncontrollable high polymers are formed. On the other hand, if growing radicals are in dynamic equilibrium with dormant species, then well-defined polymers may be prepared.

There are several systems which provide well-defined polymers by radical polymerization. They are based on the same principle of establishing dynamic equilibrium between dormant species and growing radicals.[1] As dormant species, alkyl dithiocarbamates,[2] alkoxyamines,[3] organometallic derivatives,[4] and alkyl halides[5] have been reported. It seems that the equilibrium position between active and dormant species is mostly affected by the structure of the alkyl group, the corresponding scavenger, and the reaction temperature.

The lability of the bond between the alkyl group and scavenger which should be homolytically (and revers-

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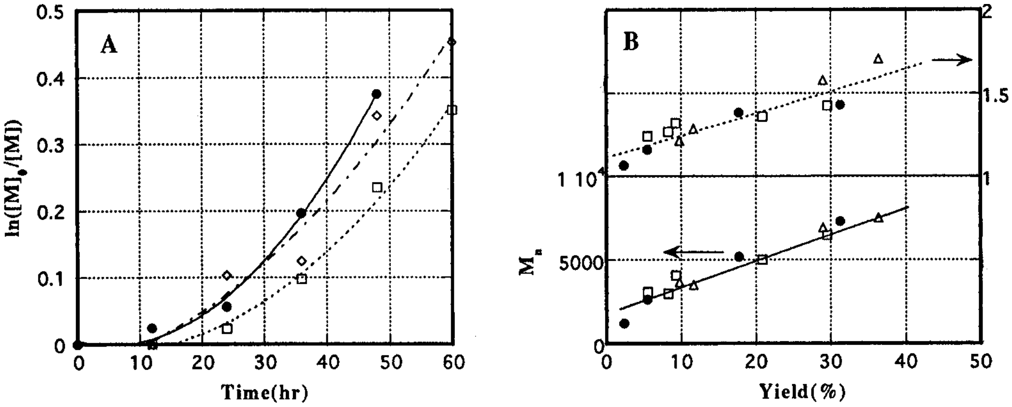


Figure 1. Bulk self-initiated polymerization of styrene with TEMPO derivatives at 120 °C ([TEMPO derivative]$_0$ = 0.03 M): (●) [G-2]-TEMPO; (□) TEMPO, (△,◇) 4-(benzyloxy)-TEMPO. (A) Kinetics. (B) Evolution of molecular weights and polydispersities with conversion.

ibly) cleaved increases with temperature and most of the controlled radical polymerizations require elevated temperature (>100 °C). Although the ratio of the rate constant of propagation to that of termination increases with temperature, leading to better control, the probability of transfer and decomposition of dormant species increases simultaneously. Thus, a temperature range must be adjusted to match the requirements of each particular system.

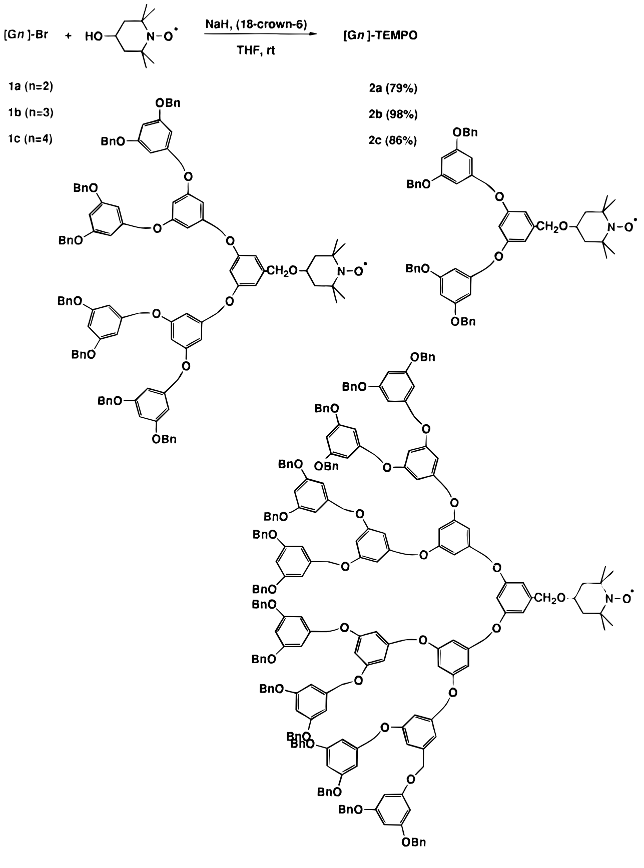
An alternative approach to decrease the rate of bimolecular termination is to use electrostatic repulsion between the growing species (as in cationic and anionic reactions), or to increase the viscosity of the medium or to reduce the rate of termination for steric reasons. Previous work has shown that initiators with increased steric requirements such as dendrimers may be used to enhance the anionic ring-opening polymerization of ϵ-caprolactone, affording dendrimer-bound polyesters of low polydispersity.[6]

In this paper, we report the preliminary results of attaching nitroxyl radical (TEMPO; 2,2,6,6-tetramethylpiperidine 1-oxyl radical) to the interior of dendrimers[7] of variable size and the use of these novel scavengers in the radical polymerization of styrene. The use of modified TEMPO as a scavenger in styrene radical polymerization could lead to better defined systems if homolytic cleavage occurs at the appropriate temperature, monomer can diffuse inside the cavity of the dendrimer, the polymer is at least partially compatible with the dendrimer, the proportion of chains generated outside the cavity by self-initiation is small and/or the exchange reactions between these chains and those connected to the dendrimers are fast, and the dendrimer does not participate in additional side reactions.

Experimental Section

Styrene was distilled under reduced pressure and was redistilled over calcium hydride under reduced pressure just prior to use. Benzoyl peroxide (BPO) and 2,2′-azobis(2-methylpropionitrile) (AIBN) were recrystallized from methanol/chloroform and diethyl ether, respectively. TEMPO-substituted dendrimers, [G-2]-, [G-3]-, and [G-4]-TEMPO, were synthesized by the reaction of 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl radical (4-OH-TEMPO) and [G-2]-, [G-3]-, and [G-4]-bromide, respectively (Scheme 1).[8] 4-Hydroxy-TEMPO was converted to its sodium salt by reaction with sodium hydride, and the product was allowed to react with the corresponding bromides in THF solution. The resulting adducts were purified by SiO$_2$ flash column chromatography.

Scheme 1



Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC), using a Waters 510 pump equipped with a 410 differential refractometer and photodiode array UV detector, with tetrahydrofuran (THF) as eluent with a flow rate of 1.0 mL·min^{-1} and with three Ultrastyragel columns (100 Å, 500 Å, and Linear) in series. The molecular weight calibration curve was obtained using ten polystyrene standards.

All polymerizations were carried out under an argon atmosphere. After polymerization was stopped by cooling to room temperature, the mixture was first diluted with small amounts of THF and then poured into methanol. Conversion was determined by GC, using a Shimadzu GC-14A with a wide-bore capillary column. The precipitated polymers were filtered and dried in vacuo at room temperature overnight. Small portions were analyzed by GPC.

In the experiments with AIBN, a mixture of TEMPO-containing dendrimers and AIBN was heated in toluene at 120 °C for 12 h to form adducts of TEMPO-substituted dendrimer with isobutyronitrile radical, and then the solvent was re-

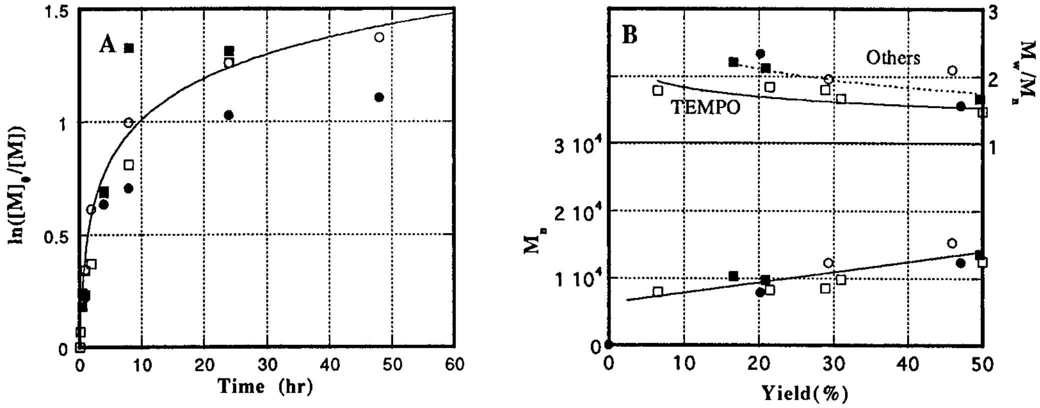


Figure 2. Bulk polymerization of styrene with TEMPO derivatives initiated by BPO at 120 °C ([TEMPO derivative]$_0$ = [BPO]$_0$ = 0.03 M); (●) [G-2]-TEMPO; (○) [G-3]-TEMPO; (□) TEMPO; (■) 4-(benzyloxy)-TEMPO. (A) Kinetics. (B) Evolution of molecular weights and polydispersities with conversion.

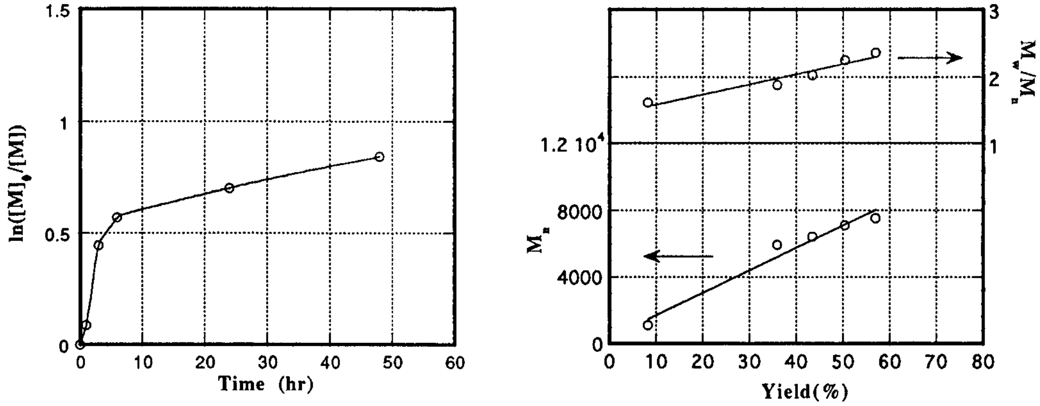


Figure 3. Bulk polymerization of vinyl acetate with [G-3]-TEMPO/AIBN adduct at 80 °C ([adduct]$_0$ = 0.03 M). (A) Kinetics. (B) Evolution of molecular weights and polydispersities with conversion.

moved in vacuo. The residue was dissolved in monomer, and the mixture was heated to the appropriate temperatures.

Results and Discussion

Polymerization of Styrene. The thermally self-initiated bulk polymerization of styrene with [G-2]-TEMPO (initial concentration [T]$_0$ = 30 mM)[9] started at 120 °C after about a 12 h induction period. This is similar to systems operating in the presence of TEMPO or 4-(benzyloxy)-2,2,6,6-tetramethylpiperidine 1-oxyl radical (4-(benzyloxy)-TEMPO) (Figure 1). These results indicate that polymerizations with [G-2]-TEMPO proceeded analogously to those with TEMPO or 4-(benzyloxy)-TEMPO. Radicals generated by thermal self-initiation of styrene[10] are quenched successfully by [G-2]-TEMPO. The quenched product undergoes reversible homolytic cleavage and the generated radicals react with monomer. The resulting growing chains are then trapped with [G-2]-TEMPO at the appropriate rate at 120 °C.

BPO-initiated bulk polymerizations with [G-2]- and [G-3]-TEMPO ([I]$_0$ = 30 mM, [T]$_0$ = 30 mM, 120 °C) showed the same tendency as those with TEMPO and 4-(benzyloxy)-TEMPO; however, the polydispersities with [G-*n*]-TEMPO were slightly higher than those with TEMPO (Figure 2). The higher polydispersity indicates potential side reactions, self-initiated polymerization of styrene outside of the dendrimers, spontaneous chain transfer, or transfer induced by benzylic hydrogen atoms inside the dendrimers.

Polymerization of Non-Self-Initiating Monomers with [G-*n*]-TEMPO. In order to prevent self-initiation, methyl methacrylate (MMA), *n*-butyl acrylate (BA), and vinyl acetate (VAc) were polymerized. These monomers do not self-initiate or self-initiation is very slow. The polymerizations were carried out after [G-*n*]-TEMPO/AIBN adducts were formed by heating a mixture of [G-*n*]-TEMPO and AIBN in toluene for 12 h at 80 °C.

In the case of methyl methacrylate ([[G-3]-TEMPO/AIBN adduct]$_0$ = 30 mM, in bulk) at 80 °C, no polymerization was observed even after 60 h. In contrast, the bulk polymerization of vinyl acetate, a monomer with less steric hindrance than methyl methacrylate, proceeded at 80 °C with [G-3]-TEMPO/AIBN adduct ([adduct]$_0$ = 30 mM), as shown in Figure 3. The kinetic data show that its polymerization proceeds faster at the early stages, but the polydispersity is higher than for styrene. A comparison with the results obtained for styrene suggests that poly(vinyl acetate), which is more polar than polystyrene, has a lower compatibility with the dendrimers, and therefore poly(vinyl acetate) growing chains are released irreversibly from the cavity of the dendrimers and slowly recombine.

This suggests that in order to control the polymerizations it is necessary to keep the growing radical chains inside the cavity of the dendrimers. Decalin, which is expected to be less compatible with poly(vinyl acetate) or poly(*n*-butyl acrylate) than the dendrimers, was therefore selected as a solvent for the polymerization of vinyl acetate and *n*-butyl acrylate, in an attempt to keep chains attached to the dendrimer.

First, the polymerization of vinyl acetate with [G-4]-TEMPO and AIBN was carried out in decalin at 80 °C ([VAc]$_0$ = 1.0 M, [[G-4]-TEMPO/AIBN adduct]$_0$ = 0.50 mM). The polymer precipitated after 30 min, and both

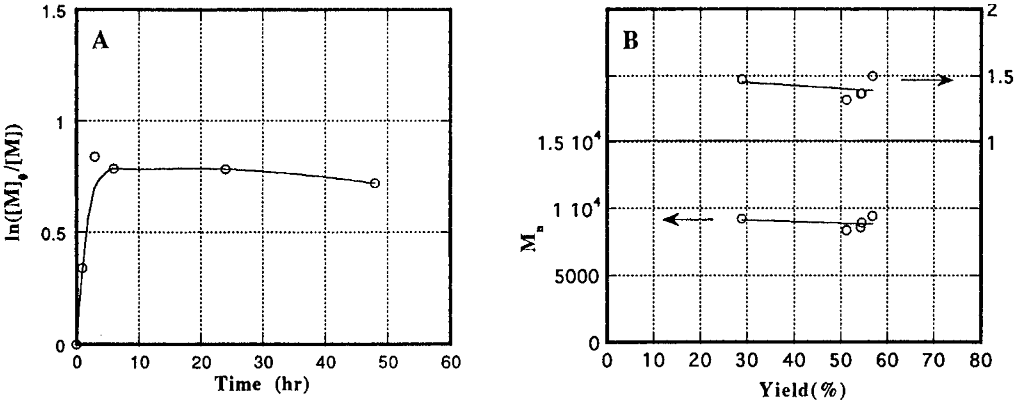


Figure 4. Solution polymerization of *n*-butyl acrylate with [G-4]-TEMPO/AIBN adduct in decalin at 80 °C ($[BA]_0 = 1.0$ M, $[adduct]_0 = 0.005$ M). (A) Kinetics. (B) Evolution of molecular weights and polydispersities with conversion.

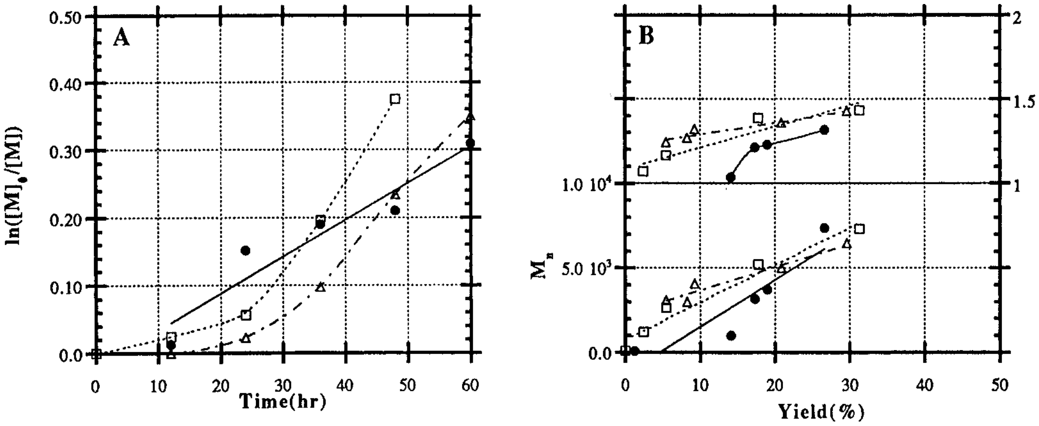


Figure 5. Polymerization of styrene with TEMPO derivatives at 120 °C ($[styrene]_0 = 8.7$ M in bulk and 3.8 M in benzyl ether, $[TEMPO\ derivative]_0 = 0.03$ M): (●) TEMPO in benzyl ether, (□) [G-2]-Tempo in bulk; (△) TEMPO in bulk. (A) Kinetics. (B) Evolution of molecular weights and polydispersities with conversion.

the polymer yield (12%) and its molecular weight did not change during later stages of the reaction (48 h). The number-average molecular weight (M_n) was about 6000, and the polydispersity was about 1.1. In the GPC measurement, [G-4]-TEMPO was observed as the species with molecular weight of about 3600, and the peak corresponding to the precipitated polymer had UV absorption, suggesting its structure as a "complex" poly(vinyl acetate)–[G-4]-TEMPO. Relatively low polydispersity may originate in monodispersed dendrimer attached to a polymer chain; however, these results might also indicate that the poly(vinyl acetate) chains could grow in a controlled manner within the cavity of [G-4]-TEMPO but that precipitation of a poly(vinyl acetate)–[G-4]-TEMPO complex occurs at $M_n \approx 6000$, thereby limiting the growth of the chains.

n-Butyl acrylate was also used as a monomer ($[BA]_0 = 1$ M, $[[G\text{-}4]\text{-}TEMPO/AIBN\ adduct]_0 = 0.005$ M, 80 °C). The results are shown in Figure 4. The kinetics indicates that polymerization terminates before 3 h. The M_n and polydispersity/conversion relations remain nearly constant, independent of the reaction time ($M_n \approx 9000$, $M_w/M_n \approx 1.4$). The polydispersity is much lower than for a typical radical polymerization of *n*-butyl acrylate. In the early stages of the process, the polymerization proceeds within the cavity of [G-4]-TEMPO; however, as the polymerization continues, the insolubility of the polymer attached to the dendrimer leads to its precipitation and termination of the growth process.

The low polydispersities obtained for both poly(vinyl acetate) and poly(*n*-butyl acrylate) suggest that the polymerization can indeed proceed in a controlled manner within the cavity of [G-4]-TEMPO, at least at the early stages of the polymerizations.

Polymerization of Styrene in the Presence of Benzyl Ether. Because the dendrimers contain benzylic hydrogens that might be abstracted by the growing radicals leading to undesired radical transfer reaction, the polymerization of styrene in the presence of benzyl ether was studied, assuming that benzyl ether is a relatively close model of the benzyl ether moieties incorporated into the dendritic structure.

The results obtained for the thermal self-initiated polymerization of styrene with benzyl ether ($[styrene]_0 = 3.8$ M, $[TEMPO]_0 = 30$ mM, $[benzyl\ ether]_0 = 3.0$ M, 120 °C) are plotted in Figure 5 together with those obtained with [G-2]-TEMPO. The rate of polymerization with TEMPO in benzyl ether is similar to that with [G-2]-TEMPO. The molecular weight of polystyrene formed in the presence of a large excess of benzyl ether is only slightly lower than that obtained with [G-2]-TEMPO. These results indicate that the contribution of transfer to benzylic hydrogens is rather small at the studied range of molecular weights. This is in agreement with the reported earlier transfer coefficient ($c_{tr} = 0.006$ at 60 °C).[11] Up to 40% conversion, the effect of benzyl ether (3 M) should lead to less than 20% reduction in molecular weights and polydispersities lower than 1.3, as observed in Figure 5.

Conclusions

The use of stable radicals attached to dendrimers of variable size was attempted to control the radical polymerization of styrene, vinyl acetate, and (meth)-acrylates. The thermal polymerization of styrene with [G-2]-TEMPO proceeds similarly to the polymerization with TEMPO alone. In the polymerization of styrene initiated with BPO, the kinetics and the molecular weight/conversion relationships showed the same tendency as with TEMPO itself, though the polydispersity was higher than without dendrimers. This indicates that homolytic cleavage occurs at the reaction temperature, the monomer can diffuse inside the cavity of the dendrimer, and the polymer is at least partially compatible with the dendrimer. Model reactions indicate that the higher polydispersities cannot be ascribed to chain transfer involving benzylic hydrogen atoms. Therefore, the higher polydispersities may be attributed to the self-initiated polymerization of styrene outside the dendrimers and the slower exchange with chains attached to the dendrimers.

To evaluate the effect of self-initiation, vinyl acetate, methyl methacrylate, and *n*-butyl acrylate were used. However, these polymers showed incompatibility with the dendrimers. As a result, the growing chains are easily released from the cavity of the dendrimers into solution, and their return to the cavities of the dendrimers is not fast enough to control the polymerization. The results of the solution polymerization in decalin indicate that the polymerization of these monomers is better controlled but only at the early stages of the polymerizations. The subsequent precipitation of polymers attached to dendrimers prevents the polymerization to higher molecular weights.

These results suggest that the main reason for the increased polydispersities is not termination between the growing chains but either the decomposition of alkoxyamines[12] or self-initiation that occurs simultaneously with the slow propagation.

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