Articles

Preparation and Thermal Properties of Enaminonitriles-Terminated Reactive Polymer Precursors

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Various enaminonitriles-terminated reactive polymer precursors containing rigid aromatic and flexible alkyl units were prepared from the corresponding diamines and 1-chloro-1-phenyl-2,2-dicyanoethene (**1**). All the enaminonitriles-terminated precursors were characterized by spectroscopies and elemental analysis. They were highly soluble in DMF and NMP, and partially soluble in common organic solvents such as THF and acetone. They showed a large exotherm around 350 °C attributable to the thermal polymerization by crosslinking of the dicyanovinyl group. Upon heating the precursors, heat-resistant and insoluble network polymers were obtained. Thermogravimetric analyses of the precursors containing rigid aromatic moiety exhibited thermal stability with a 10% weight loss around 420-480 °C and 75-88% residual weight at 500 °C under nitrogen.

Introduction

The reactive oligomers approach has served as an attractive route to high performance and high temperature materials for a variety of application. The end-capped reactive oligomers have important advantages over previously developed high molecular weight linear polymer system. They provide processible materials with better solubility and wettability, lower melt or softening temperature. The cured products have high thermal stability and exhibit good mechanical properties after exposure to humidity. And the resins are cured through an addition reaction, so no volatile by-products are evolved giving a voidless final matrix. These properties make end-capped reactive oligomers especially attractive for matrix resin for composite materials and protective and insulating coatings for microelectronic applications.[1,2,3]

Dicyanovinyl group has been employed as one of the effective thermally curable functionalities.[4-12] The introduction of dicyanovinyl units into polymers enhanced the thermal stability as well as the solubility in common organic solvents.[4,5]

An approach to the preparation of dicyanovinyl-terminated oligomers was first reported by Mikroyannidis.[13] The concept has involved synthesis of polymer precursors consisting of rigid rod units capped at both ends with crosslinking moiety such as dicyanovinyl group. The chemical structure between the terminal groups affects the properties of the oligomers obtained and thus affords a possibility to tailor the processability of the material.

In conjunction with a study of rigid rod polymers as potential reinforcements for thermoset matrices, the synthesis and characterization of enaminonitriles-terminated reactive polymer precursors and their thermal stability of the cured polymers are the subject of this article.

Experimental

1-Chloro-1-phenyl-2,2-dicyanoethene (**1**) was prepared by the method previously reported.[6] Various diamine derivatives were prepared by the modified method described in the literature.[14] 1,4-Diazabicyclo[2,2,2]octane (DABCO) was used without further purification. *N*-Methyl-2-pyrrolidinone (NMP) was purified by vacuum distillation after drying over calcium hydride.

All melting points were determined on a Aldrich Mel-Temp II melting point apparatus using capillary tubes and are uncorrected. The solubilities of oligomers were estimated by dissolving 5 mg of powdery sample in 1 mL of solvent. Fourier-transform infrared (FT-IR) spectra were obtained with a Midac Model M-1200 spectrophotometer and ^{1}H NMR spectra were recorded on a Varian Gemini-2000 spectrometer operating at 200 MHz. Elemental analyses were performed using a Yanaco MT-3 CHN instrument. Gel fraction of the cured sample was measured by weighing the insoluble portion after filtering the solution of the cured sample in NMP through sintered glass filter. Differential scanning calorimetry (DSC) measurements were performed on a DuPont 2100 under nitrogen at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) measurements were carried out on a Mettler thermal analyzer at a heating rate of 10 °C/min under nitrogen.

Representative reaction of 1 with aromatic diamines. In a three necked round bottomed flask equipped with a dropping funnel, a condensor and a nitrogen inlet system, a solution of 4.24 g (10.0 mmol) of 4,4′-bis(*p*-aminobenzoyloxy)biphenyl and DABCO (3.70 g, 33.0 mmol) in 50 mL of dry NMP was placed. After the solution was purged with nitrogen, a solution of 3.77 g (20.0 mmol) of 1-chloro-1-phenyl-2,2-dicyanoethene (**1**) in 10 mL of NMP was added dropwise at 20 °C for 30 min. The

mixture turned yellow and reacted at 70 °C for 18 h. The reaction mixture was then cooled to room temperature and poured into an ice water. The precipitated powder was filtered, washed with methanol and water, then dried *in vacuo* at 100 °C for 20 h to yield the yellowish powder.

Other enaminonitriles-terminated polymer precursors containing arylate, aramide, imide and flexible alkyl ester and ether units were prepared by reacting **1** with the corresponding diamine derivative by similar reaction procedures.

2: Yield 78%. IR (KBr): 3270 (N-H), 3125 (C-H), 2212 (C≡N), 1735 (C=O), 1578 (C=C), 1320-1120 (C-O and C-N) cm $^{-1}$. ^{1}H NMR ($CDCl_3$): δ 8.6 (br, 2H, 2 NH), 7.6 (m, 10H, 2 -Ph), 7.8-7.0 (m, 16H, 2 -NH-Ph-CO- and -O-Ph-Ph-O-). Anal. Calcd for $C_{46}H_{28}N_6O_4$: C, 75.82%; H, 3.85%; N, 11.54%. Found: C, 75.27%; H 3.58%; N 11.46%.

3: Yield 60%. IR (KBr): 3255 (N-H), 3120 (C-H), 2212 (C≡N), 1735 C=O), 1582 (C=C), 1325-1110 (C-O, C-S and C-N) cm $^{-1}$. ^{1}H NMR ($CDCl_3$): δ 8.5 (br, 2H, 2 NH), 7.5 (m, 10H, 2 -Ph), 7.8-6.7 (m, 16H, 2 -NH-Ph-CO- and -Ph-S-Ph-). Anal. Calcd for $C_{46}H_{28}N_6O_4S$: C, 72.63%; H, 3.68%; N, 11.05%. Found: C, 72.29%; H, 3.46%; N, 11.21%.

4: Yield 78%. IR (KBr): 3325, 3250 (N-H), 3120 (C-H), 2210 (C≡N), 1730, 1678 (C=O), 1582 (C=C), 1320 (S=O), 1125 (C-S), 1320-1210 (C-O and C-N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 10.3 (br, 2H, amide 2 NH), 8.5 (br, 2H, 2 NH-C(Ph)=C(CN)$_2$), 7.5 (m, 10H, 2 -Ph), 7.8-6.7 (m, 16H, 2 -NH-Ph-CO- and -NH-Ph-SO_2-Ph-NH-). Anal. Calcd for $C_{46}H_{30}N_8O_4S$: C, 68.15%; H, 3.70%; N, 13.83%. Found: C, 67.86%; H, 3.96%; N, 13.49%.

5: Yield 74%. IR (KBr) : 3310, 3250 (N-H), 3130 (C-H), 2215 (C≡N), 1780, 1690, 1635 (C=O), 1582 (C=C), 1330-1160 (C-O and C-N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 10.5 (br, 2H, amide 2 NH), 8.5 (br, 2H, 2 NH-C(Ph)=C(CN)$_2$), 7.5 (m, 10H, 2 -Ph), 8.0-6.8 (m, 22H, 2 -N-Ph(CO)$_2$O, -N-Ph-O-Ph-N- and 2 -NH-Ph-CO-). Anal. Calcd for $C_{62}H_{34}N_{10}O_7$: Calc. C, 72.23%; H, 3.30%; N, 13.59%. Found: C, 71.92%; H, 3.22%; N, 13.26%.

6: Yield 63%. IR (KBr): 3247 (N-H), 3120 (C-H), 2855 (aliphatic C-H), 2210 (C≡N), 1732 (C=O), 1580 (C=C), 1320-1220 (C-O and C-N) cm $^{-1}$. ^{1}H NMR ($CDCl_3$): δ 8.5 (br, 2H, 2 NH), 7.5 (m, 10H, 2 -Ph), 7.8-6.8 (m, 8H, 2 N-Ph-CO-), 3.9 (t, 4H, 2 -O-CH_2-), 1.5 (m, 8H, -$CH_2CH_2CH_2CH_2$-). Anal. Calcd for $C_{40}H_{32}N_6O_4$: C, 72.73%; H, 4.85%; N, 12.73%. Found: C, 72.47%; H, 4.58%; N 12.49%.

7: Yield 78%. IR (KBr): 3265 (N-H), 3150 (C-H), 1875 (aliphatic C-H), 2212 (C≡N), 1734, (C=O), 1580 (C=C), 1320-1120 (C-O and C-N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.5 (br, 2H, 2 NH-C(Ph)=C(CN)$_2$), 7.5 (m, 10H, 2 -Ph), 7.9-6.8 (m, 16H, 2 -NH-Ph-CO- and 2 -CO-Ph-O-), 3.9 (t, 4H, -O-$CH_2CH_2CH_2CH_2CH_2CH_2$-O-), 1.5 (m, 8H, -$CH_2CH_2CH_2CH_2$-). Anal. Calcd for $C_{54}H_{40}N_6O_8$: C, 72.00%; H, 4.44%; N, 9.33%. Found: C, 72.21%; H, 4.27%; N, 9.19%.

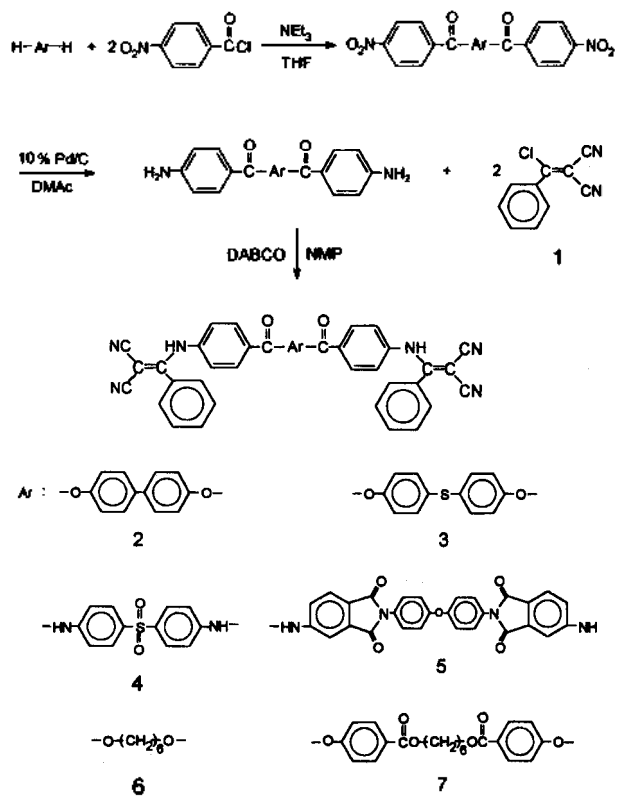
Results and Discussion

Various diamine derivatives were prepared by reacting aliphatic or aromatic diols, and diamines with *p*-nitrobenzoyl chloride, followed by catalytic hydrogenation with 10% Pd/C under hydrogen pressure (50-60 psi).[14]

Vinylic nucleophilic substitution reaction of 1-chloro-1-phenyl-2,2-dicyanoethene (**1**) with aromatic amines proceeded in high conversion to form enaminonitriles *via* addition-elimination step. Various dicyanovinyl end-capped polymer precursors including bis[*p*-(1-phenyl-2,2-dicyanovinylamino)phenyl]terephthalate and 1,5-bis(1-phenyl-2,2-dicyanovinylaminophenoxy)pentane have been previously reported.[12,15]

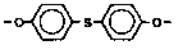
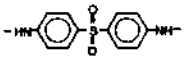
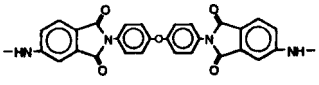
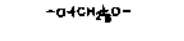
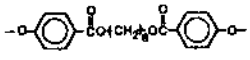
The polymer precursors bearing arylate, aramide, imide and alkyl ester as well as terminal dicyanovinyl groups were prepared as illustrated in Scheme 1. The reaction of **1** with aromatic diamines such as 4,4′-bis(*p*-aminobenzoyloxy) biphenyl, 4,4′-bis(4-aminobenzoyloxy)thiodiphenol, *N,N′*-sulfonyldiphenylenebis(*p*-aminobenzamide), 1,6-bis[*p*-aminobenzoyloxy)hexane and 1,6-bis[4-(*p*-aminobenzoyloxy) benzoyloxy]hexane were conducted in NMP solution to give the polymer precursors **2-7** in the presence of an acid acceptor, DABCO. The results of the end-capping reaction are summarized in Table 1. The reaction of 2.2 molar quantity of **1** with aromatic diamines at 60 °C was rapid and led to moderate yield of enaminonitriles-terminated reactive polymer precursors.

The chemical structures of polymer precursors were characterized by common spectroscopic techniques such as FT-IR, ^{1}H NMR and elemental analysis. The experimental results except elemental analysis are in good agreement with the structure obtained on the synthetic route. In the Infrared spectra, all the precursors showed characreristic absorption bands around 3250, 2210 and 1580 cm^{-1} corresponding to N-H, C≡N and C=C linkage. In the case of polymer precursors **2**, **4** and **5** bearing with arylate, aramide and imide-amide moieties, the characteristic absorption bands were exhibited at 1720, 1625 and 1780 cm^{-1} as-



Scheme 1.

Table 1. Results and Conditions of Preparation of Enaminonitriles-terminated Precursors

Precursor	Chemical Structure -NH-Ph-CO-X-CO-Ph-NH	Yield in %	mp in °C
2		78	282
3		60	249
4		78	–
5		74	290
6		63	188
7		78	158

*temprature 60 °C, time 18 h, solvent NMP.

signable to C=O, respectively.

In the ^{1}H NMR spectrum of precursor **2**, the aromatic protons in fragment of **1** and aromatic protons in benzoyl moiety appeared at 7.5 and 7.5-6.8 ppm as a multiplet, respectively, whereas the N-H protons of enaminonitrile appeared between 8.0-9.0 ppm as a broad band. The C/H/N ratio checked by elemental analysis gave somewhat discrepancies becaused of the impurities of polymer precursors. Actually the oligomers were purified only by successive washing with boiling methanol or ethanol because of difficulties in recrystallization.

The solubility of the precursors was tested in various solvents such as DMF, DMAc, NMP, acetonitrile, THF, acetone and ethanol. Introduction of the rather bulky and polarizable dicyanovinyl groups into rigid aromatic backbones seems to result in the good solubility of these precursors. A series of polymer precursors could be dissolved in common organic solvents including THF and pyridine as well as typical polar aprotic solvents such as DMF and NMP while they displayed virtually no solubilities in ethanol. The solubility of oligomers **6** and **7** derived from alkyl-containing diamines were found to be better than **2** and **3**, and this may be attributed to the flexibility of the chemical structure. They were even soluble in boiling THF and acetone.

DSC data of enaminonitriles-terminated polymer precursors summarized in Table 2 showed a melting transition followed by an exotherm. The DSC curves of all the precursors except **4** show endotherms, which are coincident with the melting temperatures determined in a capillary tube. DSC analysis also did detect a broad and large exothermic transition starting near 290 °C and reaching the maximum intensity around 350 °C as shown in the Figure 2. The exotherms are presumably due to the crosslinking reaction of the dicyanovinyl group. They may also arise by partial decomposition in the case of alkyl-containing precursors **6** and **7**. The initial temperature of polymerization was noted for all the samples. The initial and the maximum temperatures of the exotherms follow the similar trend regardless of the chemical structures of the polymer precursors.

TGA analysis of these precursors showed no loss in weight around 350 °C. The solubilities of the cured samples at 330 °C for 30 min reduced apparently in the solvents such as DMF and NMP, which are good solvents for the uncured precursors. This solubility decrease of the cured samples after heating seems to be caused by the considerable cross-linking of dicyanovinyl group. The precursors showed gel fraction ranging 65-93%.

When the heated samples were cooled and rescanned in

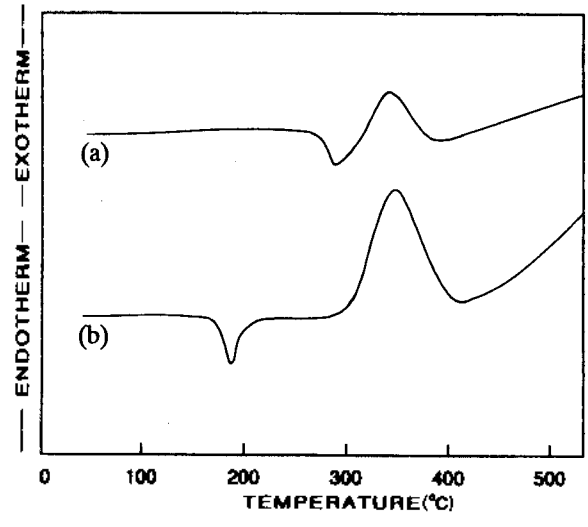


Figure 1. DSC thermograms of oligomers (a) **2** and (b) **6** at a heating rate of 10 °C/min in nitrogen.

Table 2. Thermal Properties of Enaminonitriles-Terminated Polymer Precursors and Cured Polymers

Oligomer	T_{exo}[a]	T_{endo}[b]	T_{id}[c]	$T_{10\%}$[d]	Gel Fraction	Residual Weight in % in °C		
	in %				in %	400 °C	500 °C	500 °C[e]
2	350	292	385	438	93	94	77	83
3	319	250	373	424	90	91	75	82
4	355	–	387	426	87	92	80	85
5	355	295	396	479	75	99	88	91
6	348	188	310	377	65	73	44	50
7	365	162	306	369	69	69	44	51

[a] T_{exo}: temperature of exotherm. [b] T_{endo}: temperature of endotherm. [c] T_{id}: initial decomposition temperature. [d] $T_{10\%}$: temperature determined at a weight loss of 10%. [e] Residual weight of cured precursors.

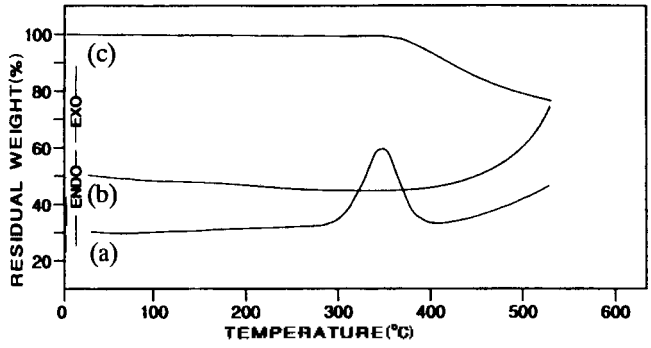


Figure 2. DSC thermograms of oligomers (a) **4** (1st scan), (b) **4** (2nd scan) and (c) TGA thermogram of **4** in nitrogen.

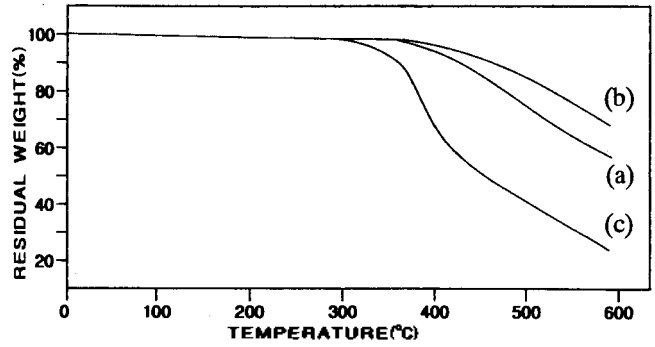


Figure 4. TGA thermograms of oligomers (a) **2**, (b) **5** and (c) **6** at a heating rate of 10 °C/min under nitrogen.

DSC analysis, the exothermic peaks were completely absent. The cured samples exhibited only large exotherms above 500 °C assignable to their thermal degradation (Figure 2(c)). The increase in the areas of the exothermic peaks of precursors **6** and **7** may be due to partial alkyl chain scission as well as the curing of the dicyanovinyl groups. Figure 3 shows the IR spectral change after the curing of precursor **3**. IR spectroscopy was used to follow the thermal curing of a sample on KBr salt plate.

In the IR spectrum, as the samples were heated, the enamine stretching bands at 3250 cm^{-1} decreased and new bands around 3400 cm^{-1} corresponding to the imine and amine appeared. At the same time, the intensity of the nitrile band around 2210 cm^{-1} decreased apparently and peaks between 1500-1600 cm^{-1} broadened. The changes in IR spectra are consistent with the the intermolecular crosslinking of most cyano groups and vinyl groups proposed previously.[6,9] It was also suggested that enamininitrile units were consumed in intramolecular cyclization.[6]

The precursors except **6** and **7** were stable up to 350 °C under nitrogen as determined by thermogravimetric analysis. The thermal stability data are listed in Table 2 and TGA traces are exhibited in Figure 3. The initial decomposition temperature (IDT) and the % residue at 500 °C were similar for the rigid aromatic precursors, and the lowest IDT and % residue were exhibited by the precursors **6** and **7**, *i.e.* 310 °C and 306 °C, and 44%, respectively. The polymers with rigid aromatic units gave a residual weight varing from 75% to 88% at 500 °C at a heating rate of 10 °C/min in nitrogen and sustained a 10% weight loss around 440 °C. Anaerobic char yields of these thermally treated dicyanovinyl containing precursors depended on their backbone structures. The precursor **5**, which contained imide units, has been found to be the most thermally stable as compared to other precursors and about 70% residual weight has been observed at 600 °C. On the other hand, the aliphatic C-H bond has a low dissociation energy and hence the aliphatic-containing polymers do not usually show high thermal stability. As can be seen from the data in Table 2, it has been found that the maximum weight loss of about 55%, takes place in alkyl-containing diamine based precursors **6** and **7**. The initial temperature of weight loss has been found in the range of 310 to 306 °C. The thermal stability of reactive oligomers is in the order **5** > **4** > **2** > **3** comparing the initial weight loss, initial degradation temperature and % residue. When the thermal properties of cured polymers at 330 °C for 30 min were compared with those of the uncured precursors, the thermal stabilities of the cured samples were improved for all the polymers in Figure 3(a). The cured resin of the the precursor **5** retains almost 90 and 72% of its mass at 300 °C and 400 °C in nitrogen over 12 h in their isothermal aging traces.

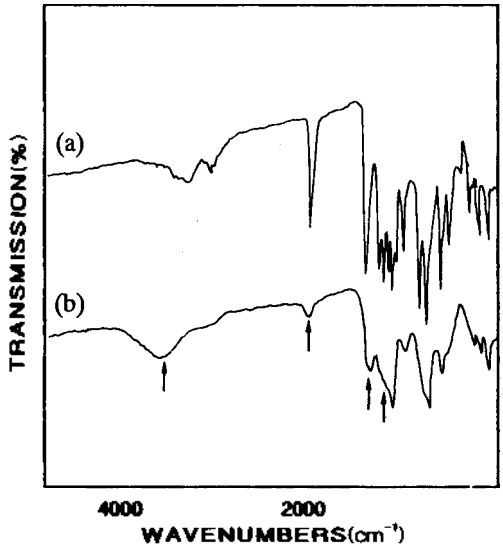


Figure 3. IR spectra of reactive oligomers **3** (a) before and (b) after heating at 330 °C for 30 min.

Though the dicyanovinyl end-capped reactive precursors exhibit reasonable thermal properties, they show lower thermal stability than polyenaminonitriles[6] or polyearyloxynitriles[7] containing dicyanovinyl groups.

More experiments on catalysts lowering the cure temperature are now in progress and the results will be presented elsewhere.

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^{13}C NMR Studies of Metabolic Pathways Regulated by HSP104 in *Saccharomyces cerevisiae*

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HSP104 protein in *Saccharomyces cerevisiae* is known to provide thermotolerance when induced by various kinds of stresses, such as a mild heat shock, ethanol, and hypoxia. It helps cells survive at an otherwise lethal temperature. Mechanisms by which HSP104 protein works are yet to be elucidated. In order to understand a molecular basis of thermotolerance due to HSP104 protein induced by a mild heat shock, studies on respiratory pathways were carried out in the wild type as well as in the *hsp104* deleted mutant. Especially the degree of ^{13}C-acetate incorporation into glutamate-C4 was examined for both strains using ^{13}C-^{13}C homonuclear spin coupling measurements, since glutamate is in a rapid equilibrium with α-ketoglutarate in the TCA cycle. In addition, the temperature effects on the rate of ^{13}C incorporation are compared with or without HSP104 protein expressed. Finally, the inhibitory effect of HSP104 on the respiration pathway was confirmed by the measurements of oxygen consumption rates for both strains.

Introduction

HSP104 plays an important role in providing thermotolerance in *Saccharomyces cerevisiae*.[1] It helps cells survive short exposures to extreme temperatures. It is expressed at a basal level at a normal temperature (25 °C) and is very strongly induced at a moderate temperature (37 °C). It is also induced by a variety of other stresses, including ethanol, arsenate, and cadmium etc.[2]

It is not still clear how HSP104 makes cells resistant against extreme heat shocks. It has been a great concern to understand a molecular basis of HSP104 function in providing thermotolerance. It was demonstrated either by electron microscopy of whole cells or *in vitro* luciferase assay that HSP104 does not function as a molecular chaperone, but instead helps cells resolublize any aggregated proteins resulting from severe heat shocks.[3] Recently, it has drawn a great attention that transient overexpression of HSP104 protein can convert cells from [*PSI*$^+$] to [*psi*$^-$], which changes a translational fidelity.[4,5] Later [*PSI*$^+$] was confirmed to be a prionlike aggregate of the cellular protein Sup35, showing that [*PSI*$^+$] altered the conformational state of newly synthesized prion proteins.[6]

Another significant aspect of HSP104 is that the hsp104 gene has been highly conserved throughout evolution.[7] The Western and Northern blot analysis revealed that the expression of HSP104 protein and the production of corresponding mRNA were significantly elevated in several organisms when exposed to heat shocks.[7] It is highly homologous to the *E. coli* ClpA/ClpB family. The other heat-inducible members of this family are also present in bacteria, cyanobacteria, flagellated parasites and plants.[8]

Interestingly, the basal level of HSP104 is higher in yeast cells grown in acetate and galactose than in cells grown in

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