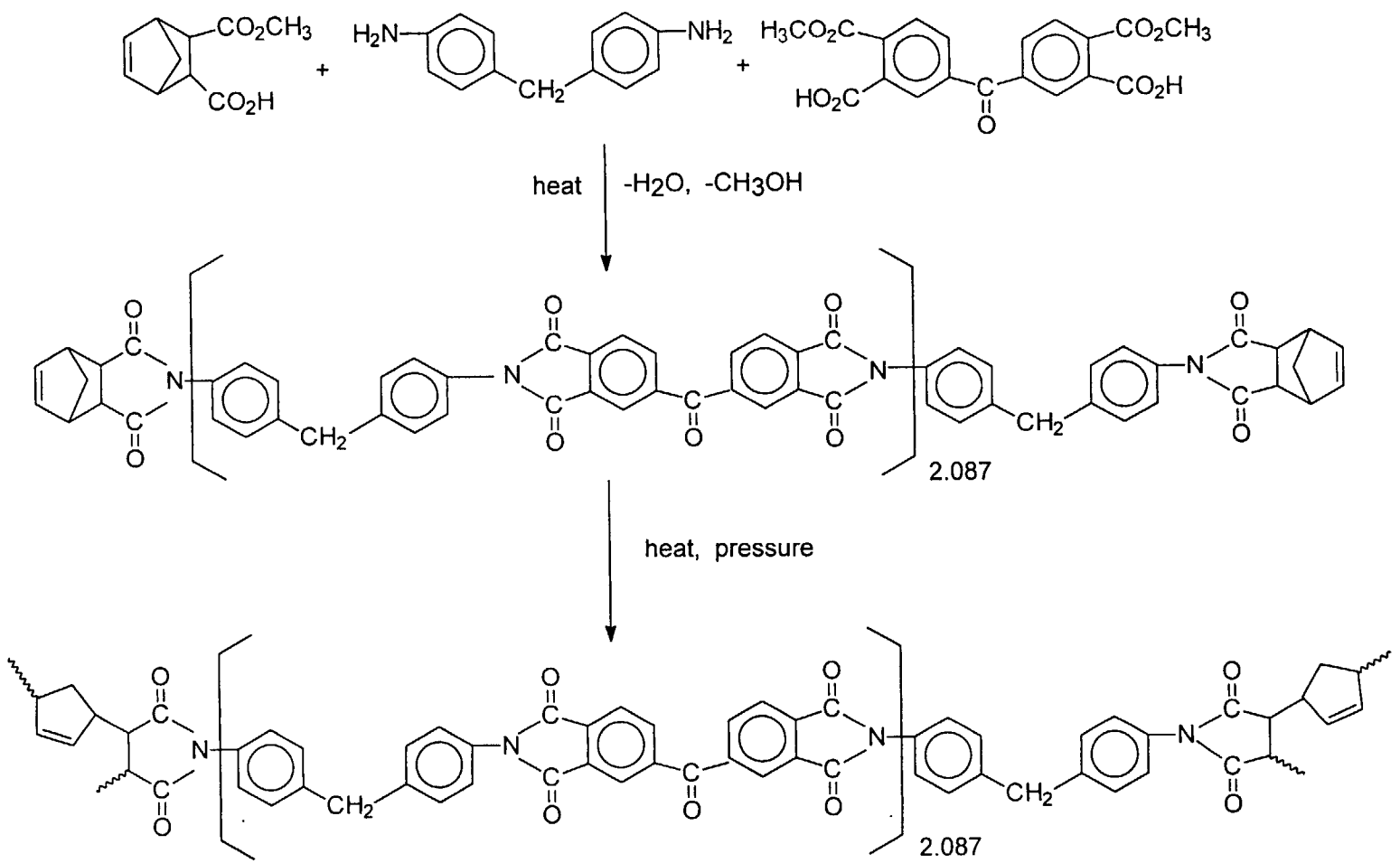
533473

Structure-Property Relationship in High T_g Thermosetting Polyimides

Kathy C. Chuang, Mary Ann B. Meador
NASA Glenn Research Center, Cleveland, Ohio 44135

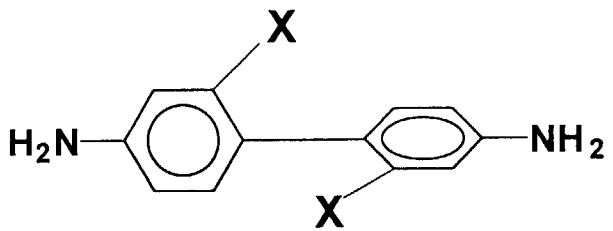
DeNise Hardy-Green
University of Akron, Akron, Ohio 44325



PMR-15

OBJECTIVE

1) Replace MDA in PMR-15 with

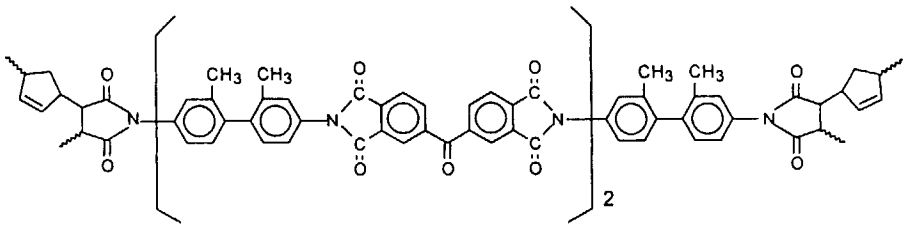


2,2'- substitued benzidine

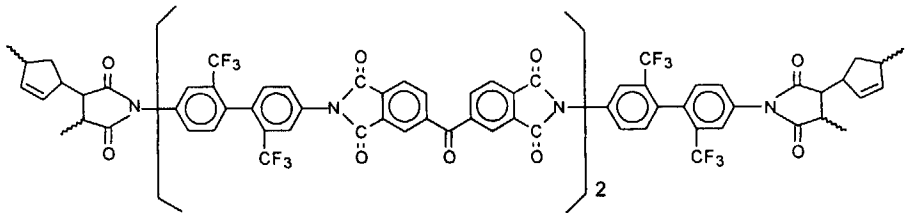
2) Evaluate the thermo-oxidative stability and

mechanical properties of DMBZ-15 against PMR-15.

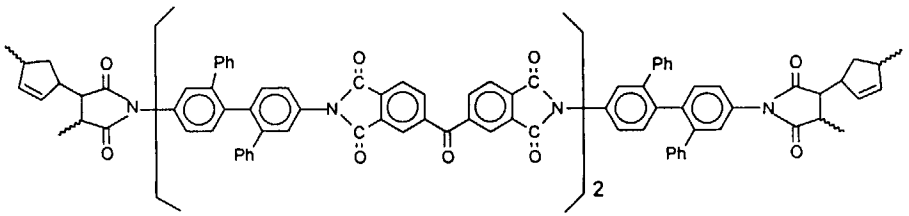
DMBZ-15



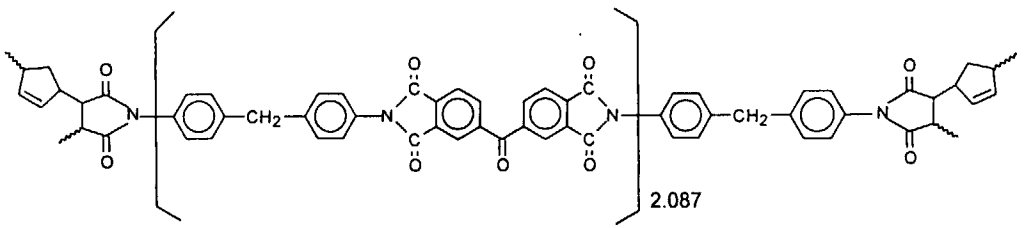
BFBZ-18



PHBZ-18



PMR-15

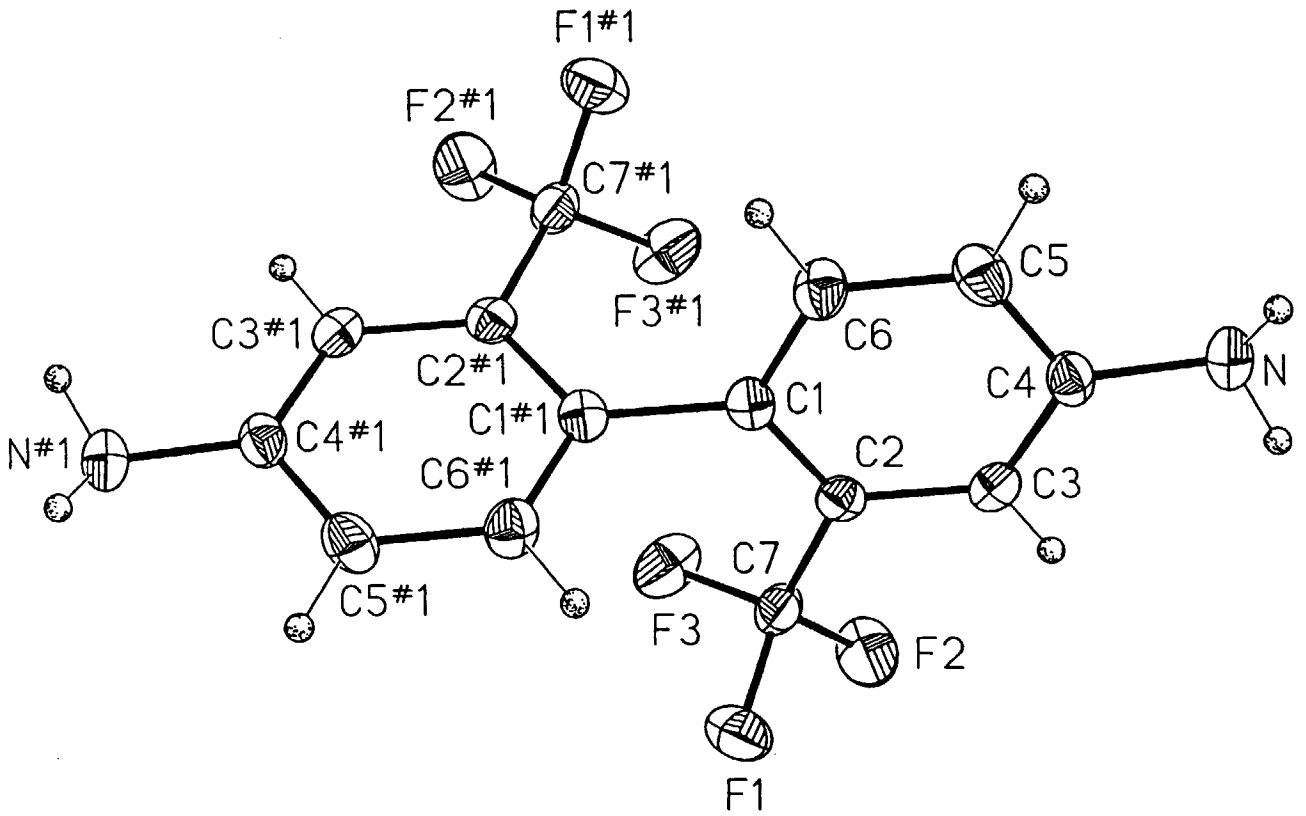


Glass Transition Temperatures (T_g's) of Polyimide Resins

Resins	T_g by TMA[a], (°C) Non-postcure	T_g by TMA, (°C) Postcure[b] at 316 °C
PMR-15	276	350
DMBZ-15	333	391
PEBZ-16	341	407
BFBZ-18	370	360[c], 404[d]
PHBZ-18	250	348

X-Ray Crystal Structure of 2,2'-Bis(trifluoro)benzidine (BFBZ)

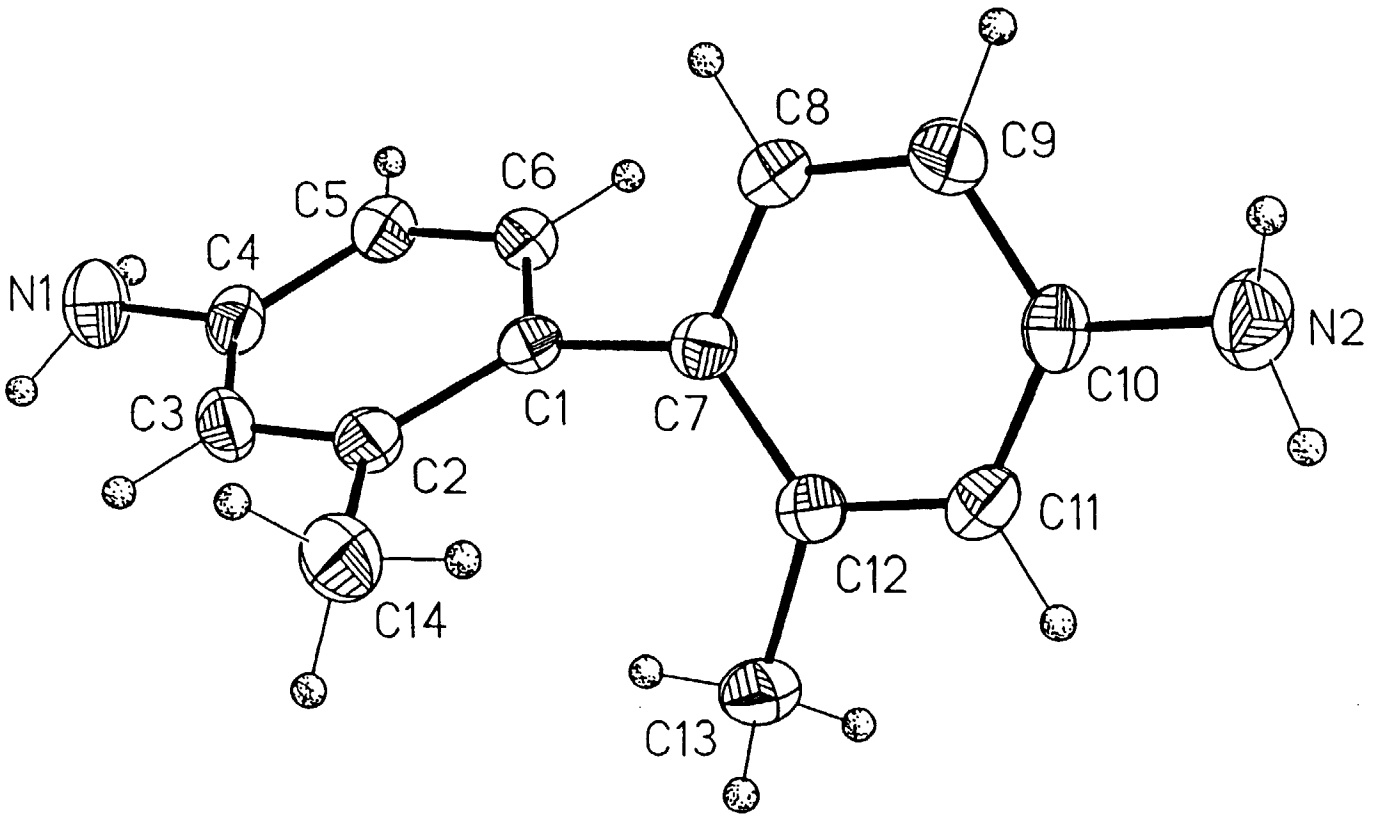
Dihedral Angle φ = 59 °



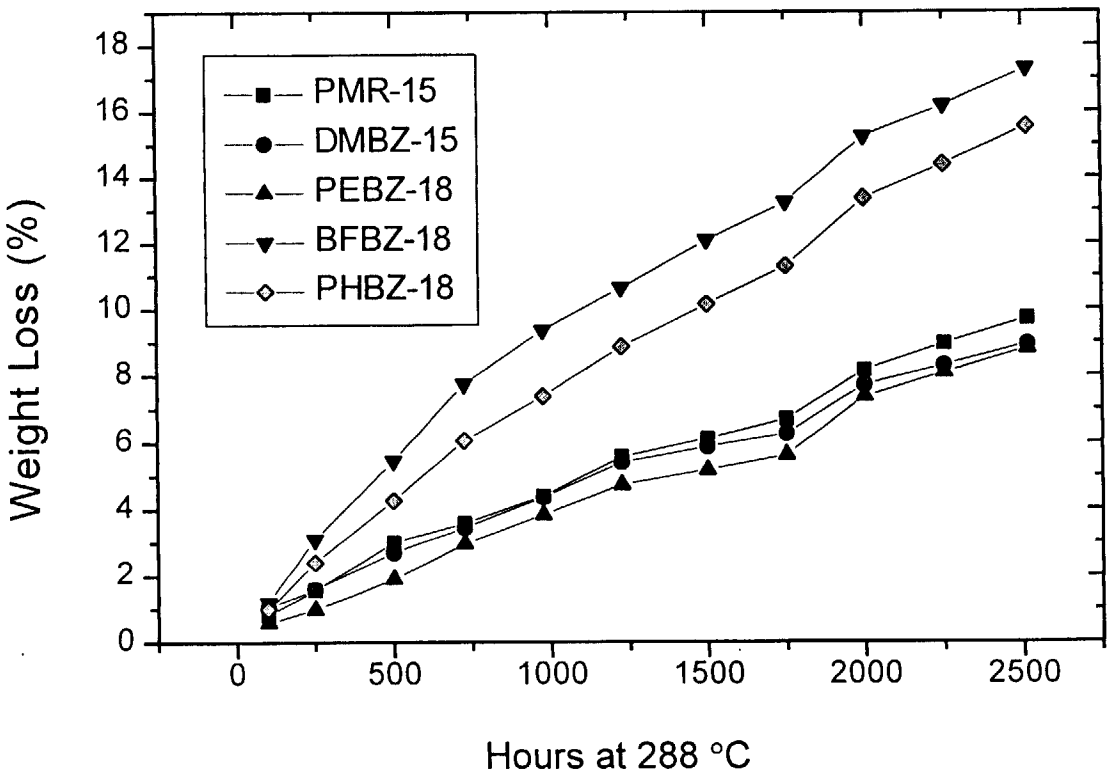
K.C. Chuang, J.D. Kinder, D. L. Hull, D.B. McConville, W.J. Youngs, Macromolecules, 30 (23), 7183 (1997)

X-Ray Crystal Structure of 2,2'-Dimethylbenzidine (DMBZ)

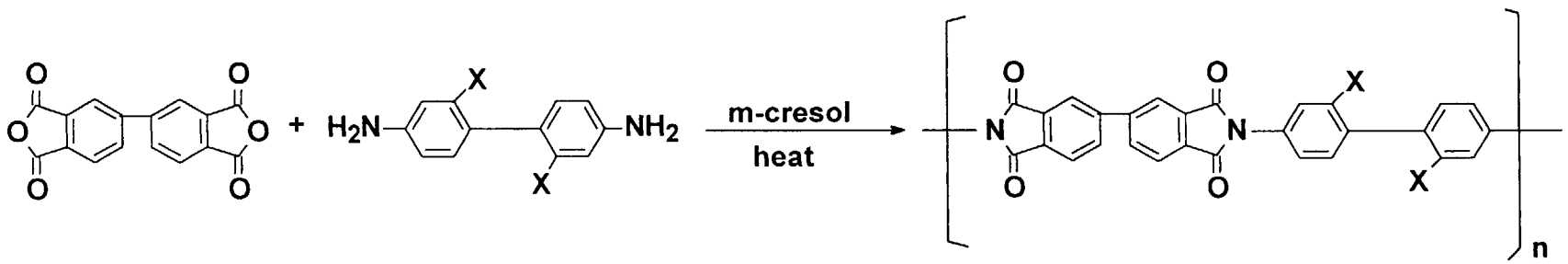
Dihedral Angle $\varphi = 75°$



Isothermal Aging of Polyimide Resins at 288 °C (550 °F) under I atm of Circulating Air



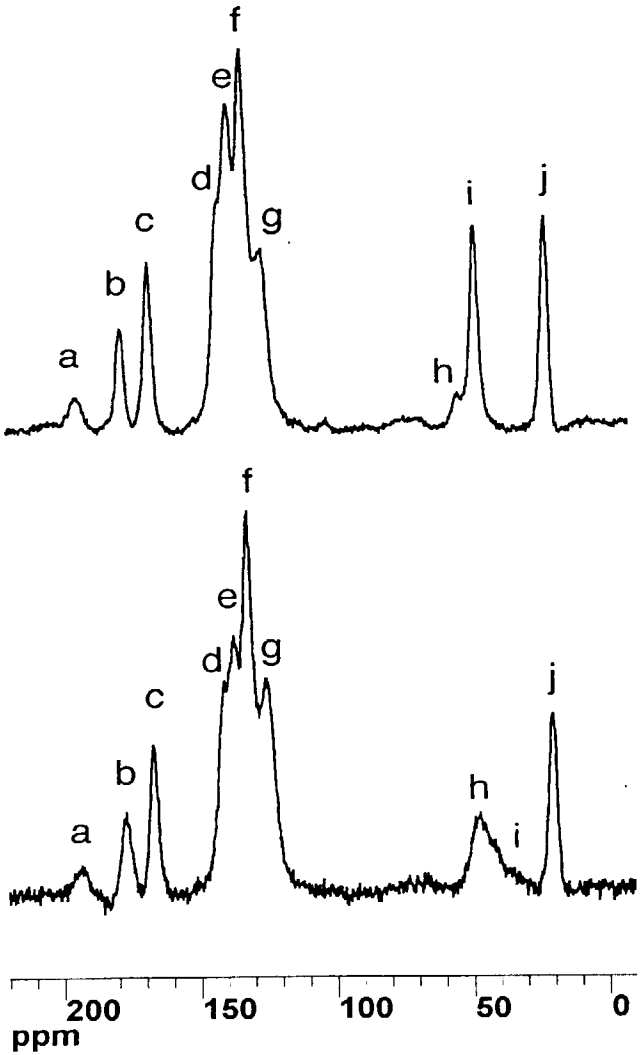
Thermoplastic Polyimides



Polyimides with Substituted Benzidine		TGA / N_2 (5% Wt Loss)
X = CF_3	T_g = 290 °C	600 °C
X = CH_3	T_g = 300 °C	500 °C
X = Ph	T_g = unclear	600 °C

Frank W. Harris, S.L.C. Hsu, c.C. Tso, Polymer Preprints, 31(1), 342 (1990)

CP-MAS ^{13}C NMR of DMBZ-15 imidized powder (top) and cross-linked resin (bottom)



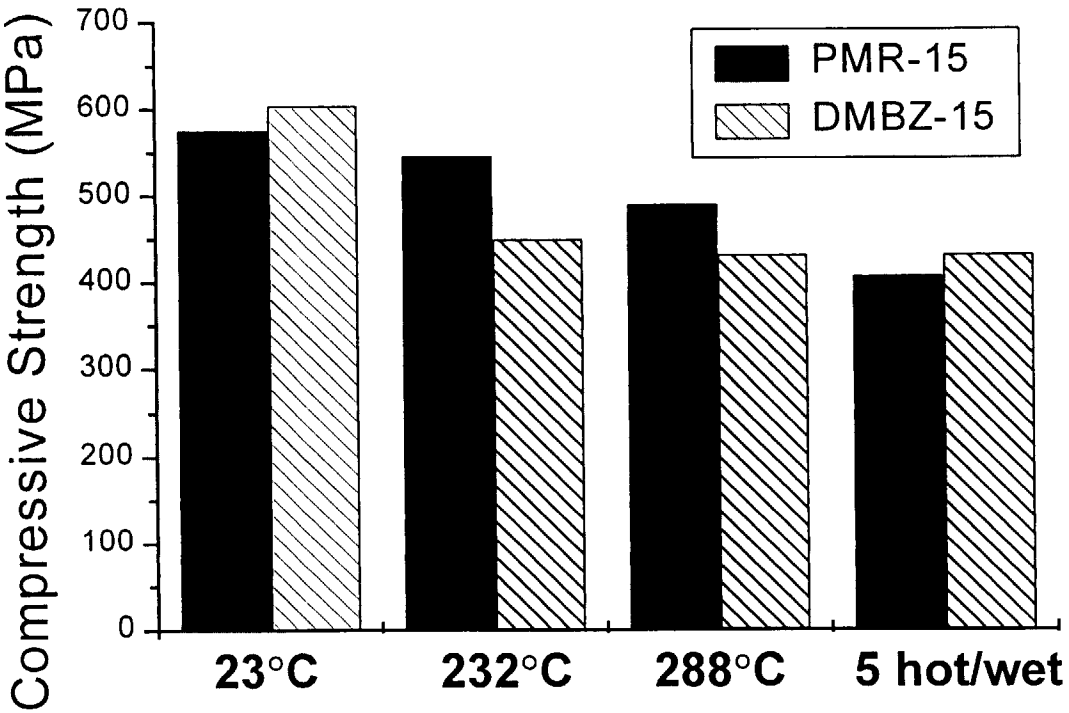
Imidized powder

a. Benzophenone carbonyl
b. Nadic imide carbonyl
c. BTDE imide carbonyl
d. DMBZ carbon next to nitrogen
e. Endcap double bond; BTDE next to benzophenone; DMBZ biphenyl link
f. Other aromatics
h. Nadic bridge
i. Other aliphatic nadic peaks
j. DMBZ methyls

Cross-linked resin (changes only)

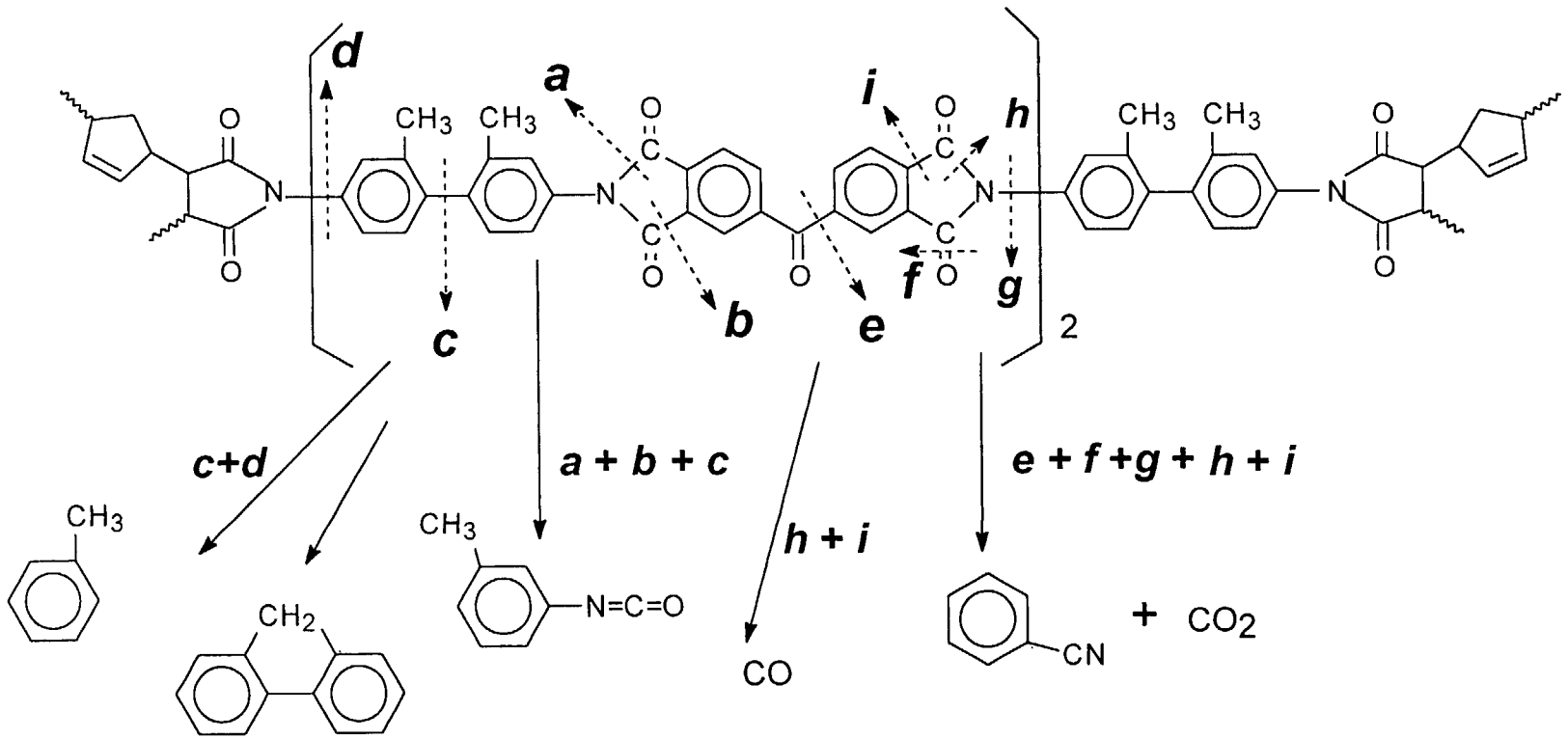
e. BTDE next to benzophenone; DMBZ biphenyl link
h. Other nadic aliphatics
i. Nadic bridge

Compressive Strength of Polyimide Composites

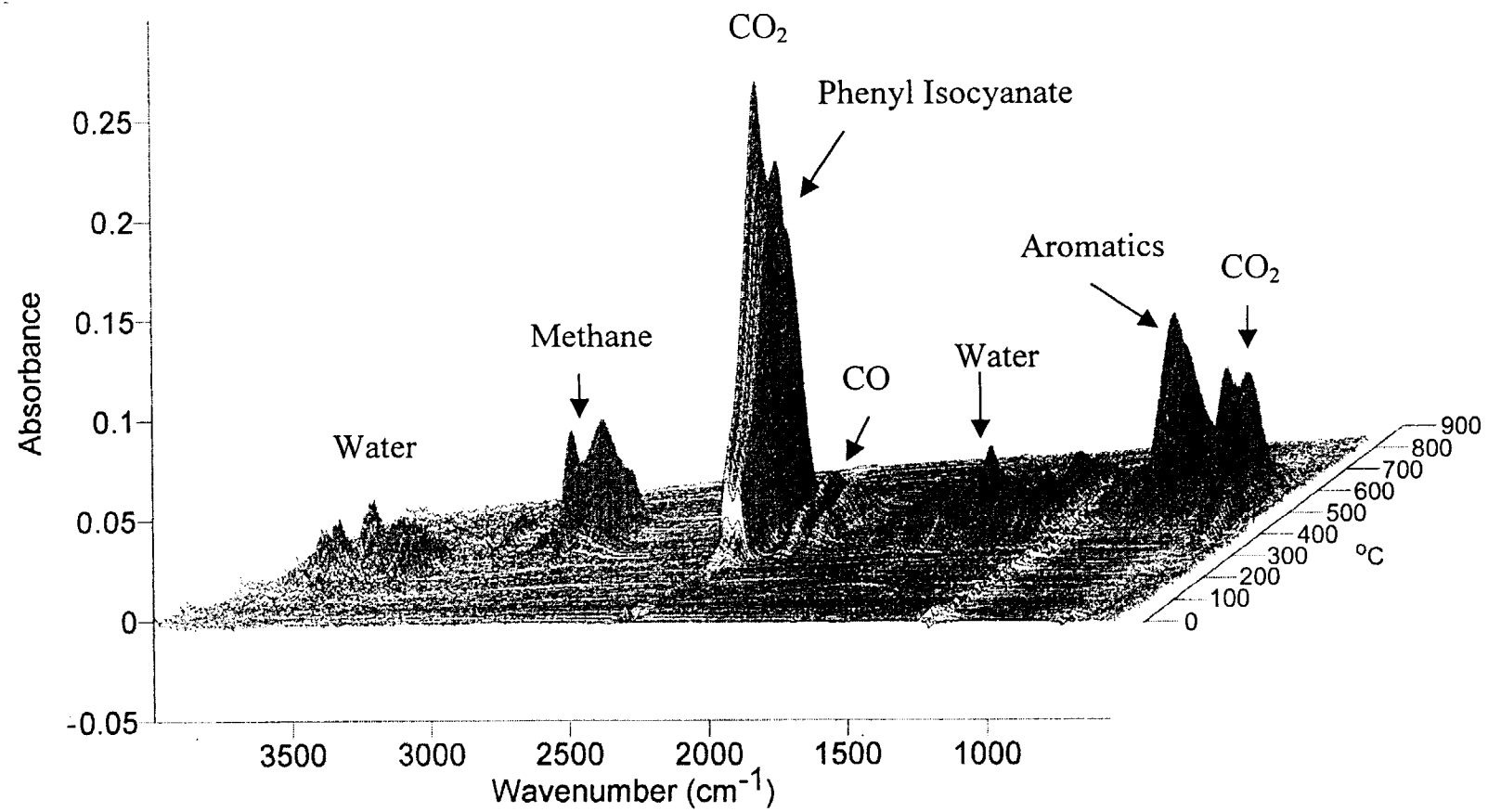


One hot-wet cycle = 93 °C water soak to >1% weight gain,
Dry out at 288 °C to < 0.1% moisture

Degradation Products of DMBZ-15 by TGA-MS



Gas Evolution Profile of DMBZ-15 Polyimide Resins



Conclusion

1) PMR polyimides containing substituted benzidines displayed high T_g's (350 – 407 °C), due to hindered rotation of noncoplanar biphenyldiamines

2) Stability of substituents in BTDA-based PMR polyimides:
$CH_3 > Ph > CF_3$, in contrast to
thermoplastic polyimdes: $CF_3 \sim Ph > CH_3$

3) Phenylethynyl endcap is more stable than nadic endcap

3) DMBZ-15 (BTDE/DMBZ/NE) composites exhibited comparable mechanical properties to PMR-15