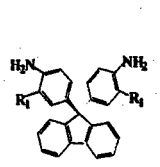
Polymer Design for Thermally Stable Polyimides with Low Dielectric Constant

Kohei GOTO

Tsukuba Research Laboratories, JSR Corporation
25 Miyukigaoka, Tsukuba, Ibaraki 305-0841, Japan
Tel: +81-298-56-2878, Fax: +81-298-56-1477, E-mail: kouhei_gotou@jsr.co.jp

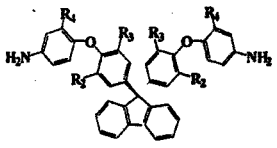
A challenge for thermally stable polymers in the field of microelectronics is lowering their dielectric constants (k). Considerable efforts have been expended in the last decade on high performance polymers including polyimides to design and synthesize new polymers with lower k for this purpose.

We performed the polymer design of polyimides with low k by introducing bulky fluorenylidene moieties (A), (B), (C). We found that among these polyimides the lowest k has been k=2.77 (@1MHz) for non-fluorinated (Ba/Cb) polyimide, and k=2.35 (@1MHz) for fluorinated one (Bg/D).



(A)

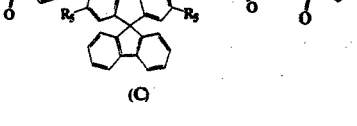
Aa: R_1=H
Ab: R_1=C_6H_5



(B)

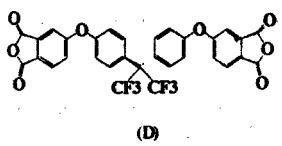
Ba: R_2=R_3=R_4=H
Bb: R_2=C_6H_5, R_3=R_4=H
Bc: R_2=H, R_3=R_4=CH_3
Bd: R_2=R_3=R_4=CH_3
Be: R_2=H, R_3=CH_3, R_4=CF_3
Bf: R_2=R_3=CH_3, R_4=CF_3
Bg: R_2=C_6H_5, R_3=H, R_4=CF_3

Based on these results, we expected that polyarylenes which are lacking a polar imide linkage might show lower k values compared with polyimides with such moieties. We successfully prepared a series of soluble, thermally stable polyarylenes by coupling polymerization of aromatic dihalides and/or bismesylates of the corresponding bisphenols using Zn and Ni-phosphine catalysts. Non-fluorinated copolyarylene (Xa/Xb=60/40) derived from bismesylates of 9,9-bis(4-hydroxyphenyl)-fluorene (Xa) and 1,1-bis(4-hydroxyphenyl)diphenylmethane (Xb) showed k=2.7 (@1MHz), Tg>300 °C, and Td (5%,N_2):549°C. The lowest k was exhibited by the fluorinated polymer with 2,2-diphenyl hexafluoropropane unit (a major chemical unit of 6FDA) (Xc), which was obtained from bismesylate of Bisphenol AF and showed k=2.2 (@1MHz), Tg: 249°C and Td (5%,N_2): 508°C.

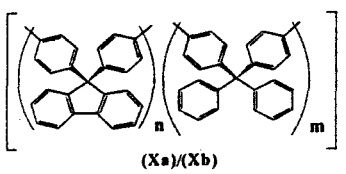


(C)

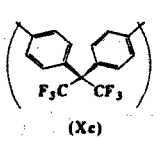
Ca: R_5=H
Cb: R_5=C_6H_5



(D)



(Xa)/(Xb)



(Xc)

Summarizing this significant information, we could make the following conclusions: 1) These polyimides with bulky fluorenylidene moieties were estimated to show the lower limit of k=2.77 for non-fluorinated polyimides and k=2.35 for fluorinated ones. 2) Soluble polyarylenes proved to be very promising as low k materials with high thermal stability. 3) Using experimental data of k *vs.* imide concentration and fluorine content in these polymers, we can estimate k value from the chemical structure of repeating unit of polyimides and polyarylenes. Thus, to achieve k lower than 2.5, it is necessary to satisfy conditionns of both 12 wt% or lower imide concentration (ca. 1170 or higher FW of repeating unit) and 10 wt% or higher fluorine content.