Thermodynamic Investigation of Polyimides by Solid-State NMR Spectroscopy and the Synthesis Novel Processable Aromatic Polyimides

Yoichi Kodama*

Product Development Laboratory, Development Center, Performance Materials Business Sector, Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura, Chiba 299-0265, Japan
Tel: +81-438-64-2485, Fax: +81-438-64-2487, E-mail: Youichi.Kodama@mitsui-chem.co.jp

1. INTRODUCTION

Polyimides are useful superengineering plastics used widely in aerospace, electronics and othe industries because of their excellent thermal stability, and their good mechanical and electrica properties. In cases where polyimides are used as thermally stable adhesives in flexible printe circuit boards and semiconductor devices, the polyimides need not only high thermal stability but als good processability, for example, low-temperature adhesion property. In order to achieve th low-temperature adhesion property, the glass transition temperature of the polyimide should be low Lately, the glass transition temperatures of polyimides can be accurately predicted by semi-empirica calculations such as the van Krevelen method. However, there have been few studies to observe th dynamics of polyimides from the viewpoint of molecular structure. This study was carried out t observe the thermal dynamics of polyimide around the glass transition temperature by solid-stat NMR spectroscopy. In addition, novel aromatic polyimides were synthesized, based on nev diamines containing flexible linkage which work effectively to lower glass transition temperatures.

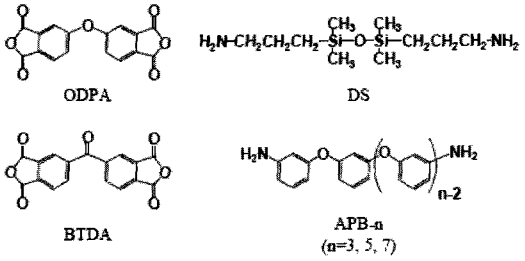
2. EXPERIMENTAL

Polyimides in this study were synthesized from tetracarboxylic dianhydrides and diamines seen i Scheme 1. The obtained solution was cast onto a glass plate and the solvent was evaporated in a oven. The film was removed from the glass plate by soaking in hot water.

Dynamic mechanical measurements were performed using a TA Instruments RSA-II at 10Hz at heating rate of 5°C/min.

DSC measurements were performed using Mac Science DSC-3110 at a heating rate of 5°C/min.

Temperature changeable solid-state ^{13}C NMR measurements were performed using Chemmagnetic CMX-300. The molecular dynamics of each carbon was evaluated by spin-lattice relaxation times T1 values using the Torchia method. T1 values were measured over a range of temperatures startin from -20 and ending at 120°C.



Scheme 1

*児玉洋一 (三井化学株式会社 機能材料事業本部 開発センター 複合技術開発部)

3. RESULTS AND DISCUSSION

Dynamic mechanical measurement results for ODPA/DS polyimide are shown in Figure 1. The peak of tanδ was 80°C, representing glass transition temperature.

Some typical ^{13}C NMR spectra at 40°C for ODPA/DS polyimide are given in Figure 2. All chemical shifts could be assigned. Signals below 50ppm came from the aliphatic DS unit, and signals above 100ppm came from the aromatic ODPA unit in ODPA/DS polyimide. From the decay behavior of NMR spectra, T1 values for all chemical shifts were estimated. The T1 values were plotted against temperature in Figure 3. This shows that T1 values of the aliphatic DS unit are moved quickly below glass transition temperature. On the other hand, T1 values of the aromatic ODPA unit are moved slowly below glass transition temperature and drastically changed around the glass transition temperature region. This result indicates that glass transition phenomena relates strongly to the mobility of the polyimide backbone and depends on the flexibility of each monomer unit used in the polyimide. This result supports the van Krevelen method which is based on the atomic group contribution hypothesis.

Using this knowledge, new meta-oriented aromatic diamines containing flexible linkage and novel aromatic polyimides, BTDA/APB-n were synthesized. The glass transition temperatures for the polyimides from DSC measurements are shown in Table 1. With an increase in the flexibility of the polyimide backbone, so the glass transition temperature became lower.

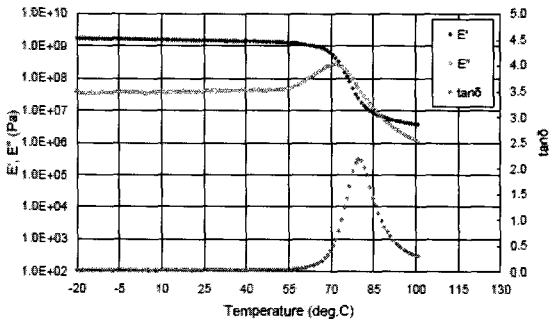


Figure 1. Dynamic mechanical measurement results for ODPA/DS polyimide.

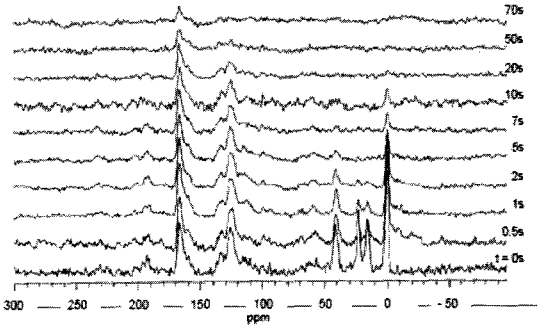


Figure 2. Decay behavior of NMR spectra at 40°C for ODPA/DS polyimide.

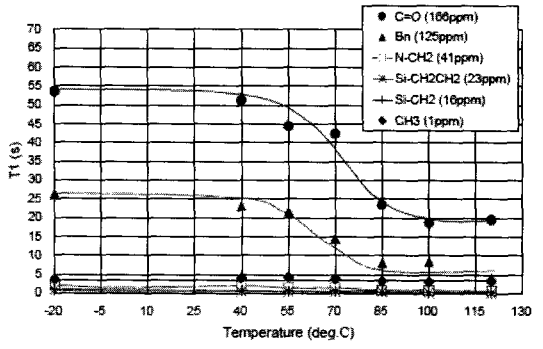


Figure 3. Temperature dependence of T1s for ODPA/DS polyimide.

Table 1. Glass transition temperatures for novel aromatic polyimides.

Polyimides	Tg/°C
BTDA/APB-3	195
BTDA/APB-5	153
BTDA/APB-7	137

4. CONCLUSIONS

Glass transition phenomena from the viewpoint of molecular structure was observed by solid-state NMR spectroscopy and novel aromatic polyimides were synthesized, based on new meta-oriented aromatic diamines which work effectively to lower glass transition temperatures.

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