Preparation and Thermal Kinetics of Poly(imide–siloxanes)

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SYNOPSIS

Thermoplastic poly(imide–siloxanes) (PISILs) were synthesized from hexafluoroisopropylidene-2,2-bis(phthalic acid anhydride) (6FDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), pyromellitic dianhydride (PMDA), and amine-terminated poly(dimethyl siloxanes) (PDMS) having different molecular weights. Glass transition temperatures of fully cured PISILs ranged from -91 to $-48°C$. Various kinetic parameters for the thermal decomposition reaction of PISILs were examined by dynamic thermogravimetric analysis (DTGA) at four different heating rates. The degradation path was a kinetically first-order reaction for PISILs (abbreviated 6FDA-860, BTDA-860, and PMDA-860, respectively) from 6FDA, BTDA, PMDA, and PDMS ($M_n = 860$ g/mol). The reaction rate constant times the half-life ($k \times t_{1/2}$) was approximately 0.693. The activation energies for decomposition were in the following order: 6FDA-860 < BTDA-860 < PMDA-860. The lifetime of the highest heat-resistant PMDA-860 at about 200°C and at the conversion level of 10% was 6.5×10^5 h or 74 years. Other kinetic factors were also calculated. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Since poly(imide–siloxanes) (PISILs) possess several advantages, such as ease of processing, a low dielectric constant, and superior adhesion, they have been recommended for microelectronic applications such as protective overcoating and used as dielectric interlayers.[1,2] PISILs are thermoplastic segmented copolymers containing a siloxane segment along the intractable backbone chain of the polyimide.[3] It is expected that these copolymers maintain some of the excellent properties of polyimide, e.g., high-temperature stability and mechanical strength, and some of the desirable properties of siloxane, such as ductility and adhesion as well as low moisture permeability.[4–6] In addition, PISILs are usually fully imidized and can be dissolved in organic solvents having a low boiling point, such as diglyme (bp 162°C). This can simplify the application process by replacing a prolonged polymer curing step at high temperature with a baking procedure at a lower one.

It requires sufficient understanding of this new material for appropriate applications.[7]

There have been several studies on the thermal degradation of poly(butadiene–acrylonitrile–acrylic acid) terpolymer, functionally terminated polybutadiene, and their cross-linked products by thermogravimetric analysis (TGA) and pyrolysis gas chromatography.[8] Hirose et al. also thermally characterized the aromatic polyethers having bis(4-fluorophenyl)phenyl phosphine oxides by Ozawa's method using TGA.[9] This practical approach to evaluate heat-resistance and thermal degradation was also applied to a variety of commercial aromatic polymers including polyimides,[10] poly(ether imide),[10] poly(ether sulfone),[10] poly(aryl ether ether ketone),[10] poly(p-xylylene),[10] and silicone polyimide manufactured by Hüls.[7] There was also an interesting report[11] that the kinetics of thermal shrinkage of the stretched polypyromellitimide (PI) films (DuPont, Kapton H) was investigated by thermomechanical analysis (TMA) at a constant heating rate. For highly stretched samples of this special rigid polymer structure with various kinds of molecular motion, the thermal contraction reaction as a function of the degree of stretching could be easily investigated using kinetic TGA.

The objective of this article was to prepare the thermoplastic PISILs from hexafluoroisopropylidene-2,2-bis(phthalic acid anhydride) (6FDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), pyromellitic dianhydride (PMDA), and poly(dimethyl siloxane) (PDMS) diamines through solution polymerization and to determine the effect of molecular weights of PDMS diamine on the thermal properties of rubbery PISILs from 6FDA and PDMS diamines. We compared the thermal stability of PISILs derived from three dianhydrides (6FDA, BTDA, and PMDA) and investigated the reaction kinetics for thermal degradation, the activation energy for decomposition, and the estimated lifetime of the above materials. Thermal stabilities of various aromatic polymers were compared with those of three PISILs as well.

THERMAL DECOMPOSITION KINETICS

There have been several methods reported for evaluating thermal stability of polymers, i.e., dynamic TGA (DTGA), static TGA, isothermal TGA/DSC, convective oven test under air or inert gas, and decomposition kinetics using DTGA. The last method, in particular, has several advantages in that this thermal test may be a time-saving technique that can be carried out using knowledge based on the reaction kinetics for 1 h to predict a century of long-term evaluation. This type of thermal evaluation of commercial products or synthesized materials is more powerful rather than the test commonly used for thermal stability and the estimation of the thermal lifetime.[12]

If simple chemical reactions are first-order decomposition or rearrangement reactions of the following type:

$$A \rightarrow B + G$$

Toop's life test theory can be applied to reaction kinetics,[13] where A is a virgin polymer; B, a degraded polymer; and G, a volatile degradation product. Then, the above chemical reaction can be considered to follow general reaction kinetics[14] or as a type of function of electrical breakdown voltage.[13] From the general reaction kinetics,

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[G]}{dt} \qquad (1)$$

$$-\frac{d[A]}{dt} = k[A] \qquad (2)$$

$$k = Z \exp(-E/RT) \qquad (3)$$

where k is a rate constant (min^{-1}), $t_{1/2}$, a half-life in minutes for thermal degradation, and Z, a preexponential factor. If the first-order reaction occurs, the reaction rate constant times half-life ($k \times t_{1/2}$) is theoretically about 0.693.[14]

If the first-order chemical decomposition occurs in a polymer system, Ozawa's integral method[8,9] and Toop's life test theory[13,15] can be utilized to predict thermal life span and activation energy for decomposition of polymer from a plot of log (heating rate = β) against the reciprocal of the temperature (T^{-1}) for a fixed degree of conversion (weight loss, %) at a different series of four or five heating rates.[8,9,15] This requires that the plotted data should produce a straight line. From the resultant thermal curves, the temperatures for a constant decomposition level can be determined. The first step in the data analysis is the choice of the level of decomposition. Typically, a value early in the decomposition profile is desired since the mechanism here is more likely to be that of an actual product failure. On the other hand, taking the value too early on the curve may result in the measurement of some volatilization (e.g., moisture or residual solvents in the sample tested) that is not involved in the failure mechanism.[15]

Flynn and Wall[16] also correlated the heating rates with the temperature for determining the activation energy of the dominant chemical reaction:

$$E = \frac{-R}{b} \left[\frac{d \log \beta}{d(1/T)} \right] \qquad (4)$$

or

$$-\log \beta_1 - 0.4567 \frac{E}{RT_1} = -\log \beta_2 - 0.4567 \frac{E}{RT_2} \qquad (5)$$

where E is an activation energy (cal/mol); R, the gas constant (= 1.987 cal/mol K); T, the temperature at a constant conversion (K); β, the heating rate (°C/min); and b, a constant (= 0.4567). R/b is about 4.35 in the range of $20 < E/RT < 60$ from Doyle's data.[17]

Toop[13] established the relationship between the estimated time to failure and the failure temperature, i.e.,

$$\ln t_f = \frac{E}{RT_f} + \ln \left[\frac{E}{\beta R} P \left(\frac{E}{RT_c} \right) \right] \qquad (6)$$

where t_f is the estimated time to failure (min); E, the activation energy (cal/mol); T_f, the failure temperature (K); R, the gas constant (= 1.987 cal/

mol K); $P(E/RT_c)$, the value taken from the numerical integration table from Toop[12]; T_c, the temperature for 5% loss at β(K); and β, the heating rate (°C/min).

Rearrangement of eq. (6) gives

$$T_f = \frac{E/R}{\ln t_f - \ln[(E/\beta R)P(E/RT_c)]} \quad (7)$$

In this work, T_c values in the range of 5–40% loss at β(K) were chosen.

EXPERIMENTAL

Reagents

Hexafluoroisopropylidene-2,2-bis(phthalic acid anhydride) (6FDA) was kindly supplied by Hoechst (Germany). 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA), and pyromellitic dianhydride (PMDA) were purchased from Aldrich Chemical Co. (U.S.A.). All anhydrides were recrystallized from acetic anhydride and dried at 170°C for 28 h *in vacuo* prior to use. 4,4'-Oxydianiline (ODA) was recrystallized from ethanol. Amine-terminated poly(dimethyl siloxanes) (PDMS, M_n = 860, 1680, 3880, and 7000 g/mol, respectively) were obtained from Shinetsu Co. (Japan) and used without any further purification. Tetrahydrofuran (THF) was dehydrated with sodium and distilled at atmospheric pressure.

Preparation of Poly(imide–siloxanes)

Figure 1 shows the synthetic scheme for the preparation of a typical polyimide prepared from 6FDA and PDMS diamines. First, 1.577×10^{-3} mol (6.30 mL) of PDMS (M_n = 3880 g/mol) was dissolved in 20.6 mL of THF at room temperature and then added dropwise with 1.577×10^{-3} mol (0.7 g) of 6FDA solution previously dissolved in 10 mL of THF through a dropping funnel for 60 min under N_2 atmosphere. The appearance of the resulting solution was white or light yellow after 24 h and it was precipitated in a mixture of methanol and water (50 : 50% in volume). The resulting rubbery siloxane poly(amic acid) (SPAA) was dried at 60°C for 48 h *in vacuo*. All PISILs were prepared by controlled thermal baking of the solution cast on the glass plate.

Characterization

Chemical structures of SPAA were confirmed by FTIR (Nicolet, Model 5DX). Inherent viscosity

(η_{inh}, dL/g) of SPAA was measured at 25°C for samples dissolved in THF (0.5 wt %) using a Ubbelohde viscometer. Glass transition temperatures and profiles of weight loss were obtained by a differential scanning calorimeter (DSC, DuPont, Model 910) and a thermogravimetric analyzer (TGA, DuPont, Model 951) attached to a thermal analyzer 2100 computer system at a heating rate of 7°C/min (DSC) under a nitrogen atmosphere (50 mL/min). In the case of TGA, heating rates were 20, 10, 5, and 2°C/min, respectively. The kinetic parameters of thermal decomposition were calculated using DuPont TGA decomposition kinetic software (Version 4.0).

RESULTS AND DISCUSSION

FTIR Analysis

Figure 2(a)–(c) exhibits the FTIR spectra for partially imidized PISILs from 6FDA and PDMS-860 cured at 100°C for 1 h (a), further cured at 155°C for 1 h (b), and at 200°C for 0.5 h (c). The rest of the PISILs were manufactured using the same thermal process. For SPAA, $\nu_{N–H}$ appears at 3500 cm^{-1}; $\nu_{C=O}$, at 1720 cm^{-1}; $\nu_{O–H}$, at 3300–2600 cm^{-1} (broad); $\nu_{C=O}$, for amide I, at 1640 cm^{-1}; and $\nu_{N–H}$, for amide II, at 1555 cm^{-1}. As SPAA was thermally cured, the band intensity of $\nu_{C=O}$ at 1778 cm^{-1} (symmetric, in-phase), $\nu_{C=O}$ (asymmetric, out-of-phase) at 1720 cm^{-1}, $\nu_{CN(CO)_2NC}$ at 1360 cm^{-1}, and the imide IV band at 715 cm^{-1} increased.[18] The intensity of $\nu_{C=O}$ (symmetric) at 1778 cm^{-1}, in particular for the imide ring, grows and does not change further at any level of thermal treatment. Therefore, during the thermal imidization step, $\nu_{C=O}$ at near 1640 cm^{-1}, attributed to the amide I band in SPAA, shifted to 1660 cm^{-1} and then gradually disappeared after the complete cycloimidization process. Characteristic peaks for the siloxane group appeared at 1259 cm^{-1} ($\nu_{Si–CH_3}$), at 802 cm^{-1} and at 1090–1020 cm^{-1} ($\nu_{Si–O}$, two strong peaks). Strong and sharp peaks near 2960 cm^{-1} ($\nu_{C–H}$) of the methylene group or methyl groups attached to silicon molecules in PDMS are shown in both SPAA and PISIL samples (see Fig. 1).

Inherent Viscosities, Solubility, and Glass Transition Temperature (T_g)

Table I lists the sample coding, inherent viscosities, yield of SPAA, and glass transition temperature (T_g) of PISILs. Inherent viscosities of PISILs ranged be-

Synthesis of Poly(imide-siloxane)

6FDA   +   **PDMS**

n = 9, 20, 50, 92

THF
RT

Siloxane Poly(amic acid) (SPAA)

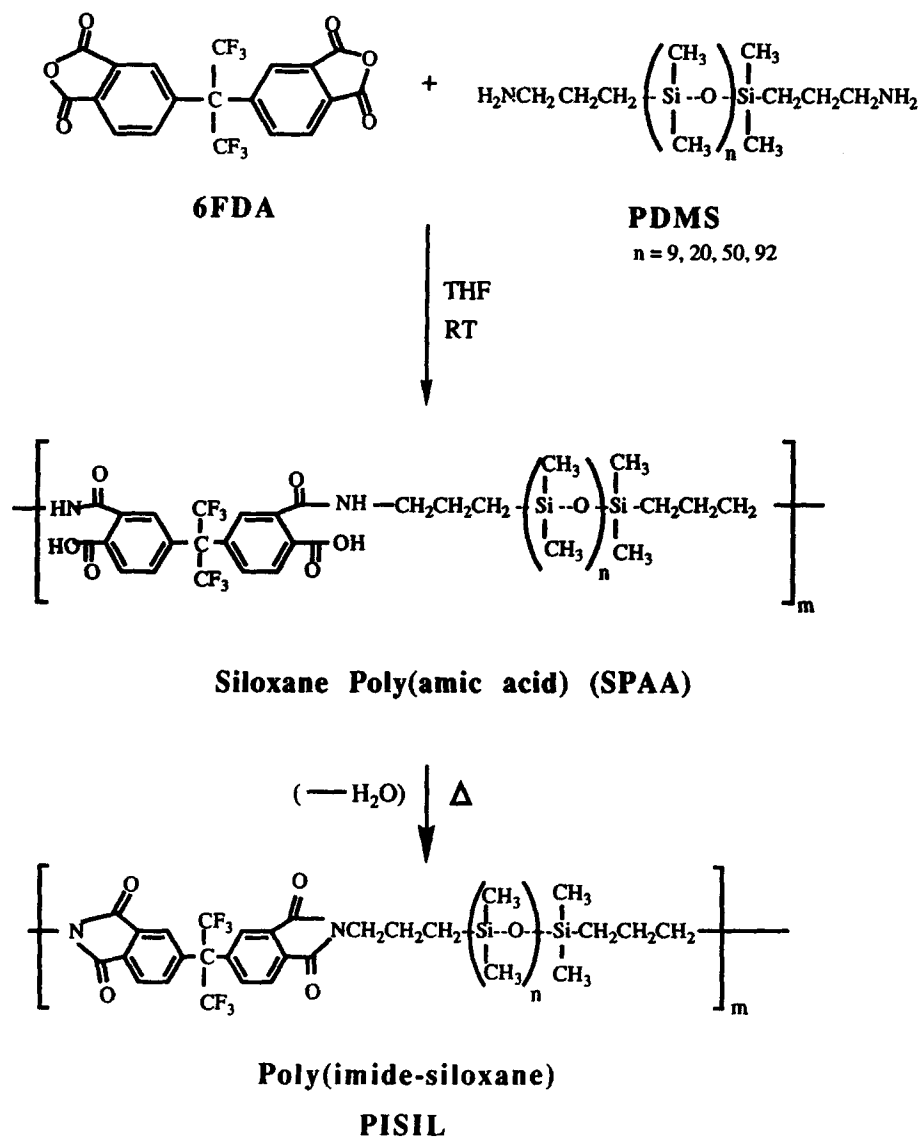(— H₂O) Δ

Poly(imide-siloxane)

PISIL

Figure 1 Synthetic schemes for the preparation of thermoplastic poly(imide-siloxane) from 6FDA-PDMS system.

tween 0.35 and 0.55 dL/g. In the DSC measurement, the following heating cycle was used for the analysis: Equilibrate at 40°C, heating rate of 30°C/min to 150°C and isothermal for 1 min at 150°C, and cool down to −160°C. All cured PISILs were scanned from −160 to 200°C (heating rate = 7°C/min, N₂ flow = 50 mL/min). One transition curve was obtained for all PISILs. T_g was taken as the midpoint of the inflection region. The glass transition temperatures measured by DSC were in the range of −91 to −48°C.

All PISILs annealed further at 300°C were soluble in THF, NMP, DMAc, DMF, CHCl₃, and toluene, whereas fully cured homopolyimides, in general, did not dissolve.[5,8,19] Such excellent solubility is caused by the tractable structure of the siloxane group, i.e., the bond length of Si — O in the flexible siloxane chain is 1.64 Å, whereas that of C — C is 1.54 Å. A bond angle of Si — O — Si is 143° and that of O — Si — CH₃ is 110°, whereas that of R — C — R (R = alkyl) is 109.5°. Therefore, a siloxane-containing polymer has a more tractable structure and
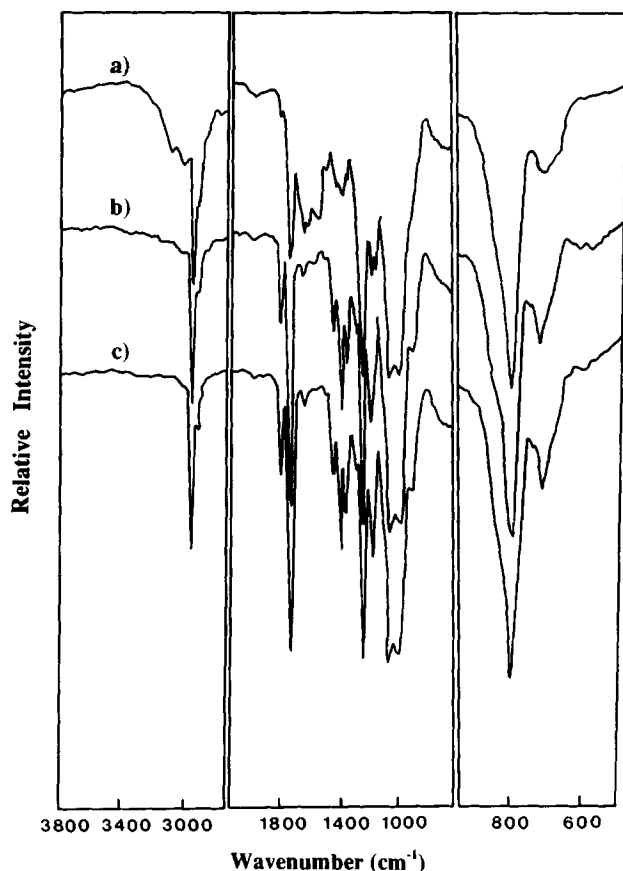
Figure 2 FTIR spectra of partially imidized siloxane poly(amic acid) and poly(imide–siloxane) from 6FDA-PDMS/860: (a) 100°C/1 h in air; (b) 100°C/1 h and 155°C/1 h in air; (c) 100°C/1 h, 155°C/1 h, 170°C/1 h, and 200°C/0.5 h in air.

less steric hindrance compared with concatenated carbon bonds of aliphatics or aromatics, resulting in a diminished molecular densification.[20]

Thermogravimetry (TGA) and Thermal Decomposition Studies

Figure 3(a) shows the TGA thermogram (heating rate = 10°C/min) for fully cured PISIL containing 6FDA and PDMS units with molecular weight ranging between 860 and 7000 g/mol. First decomposition temperatures start at around 400°C for all the samples. 6FDA-860 shows the highest temperature (467°C) for 10% weight loss. The lowest thermal stability was recorded for 6FDA-7000. We can assume that the higher the molecular weight of PDMS incorporated the lower the imide contents in unit length of PISIL. That is why the higher molecular weight PDMS unit in PISIL lowers the heat resistance.

Figure 3(b) compares the TGA thermograms (heating rate = 20°C/min) for three fully imidized PISILs from PDMS-860 and three different aromatic dianhydrides. All three samples decomposed at around 450–500°C. To evaluate the thermal stability, we selected the T_c value from 5 to 40% [see eqs. (6) and (7)]. T_c values below 5% weight loss had a slight deviation, but the degradation reaction over 5% weight loss continued constantly and thus reaction kinetics was investigated. As can be seen, thermal stabilities of PISILs are in the following order: PMDA-860 > BTDA-860 > 6FDA-860 in the range of 10–40% weight loss. The temperature for 10% weight loss of the above three PISILs was 483, 475, and 467°C, respectively. PMDA-860 was expected to show the best thermal stability because of the rather compact and symmetrical structure of PMDA in the backbone. BTDA contains a carbonyl group between aromatic rings that acts in lowering the thermal stability. 6FDA possesses a rather bulky hexafluoroisopropylidene unit and can be easily de-

Table I Sample Coding, Inherent Viscosity, T_g, and Yield of Poly(imide–Siloxanes)

Synthetic System[a]	Code	η_{inh}[b] (dL/g)	T_g[c] (°C)	Yield[d] (Wt %)
6FDA–PDMS/860	6FDA-860	0.40	−82	93
6FDA–PDMS/1680	6FDA-1680	0.35	−73	87
6FDA–PDMS/3880	6FDA-3880	0.46	−91	91
6FDA–PDMS/7000	6FDA-7000	0.55	−48	96
BTDA–PDMS/860	BTDA-860	0.41	−84	93
PMDA–PDMS/860	PMDA-860	0.42	−86	90

[a] Nos. after PDMS are the molecular weights of poly(dimethyl siloxane diamines).
[b] Measured in THF at 25°C; concentration of SPAA = 0.5 wt %.
[c] T_g of PISILs run by DSC (see Experimental section).
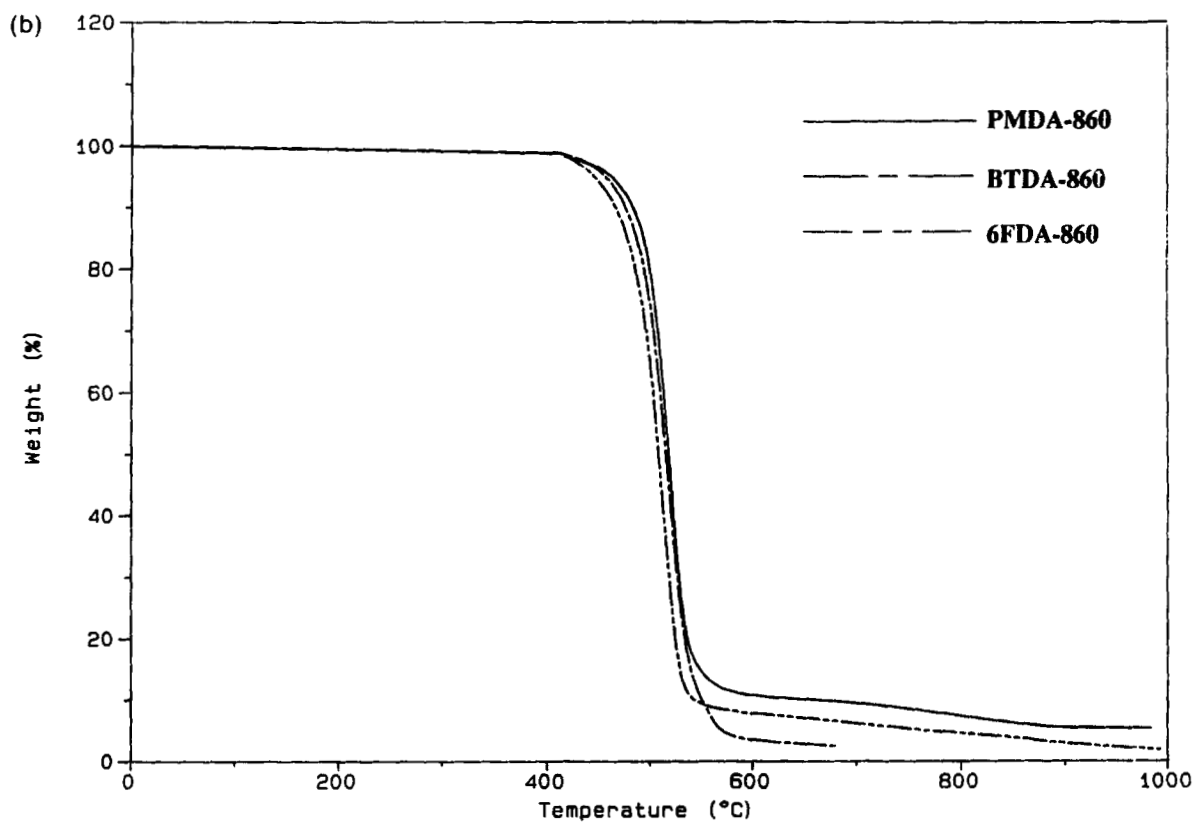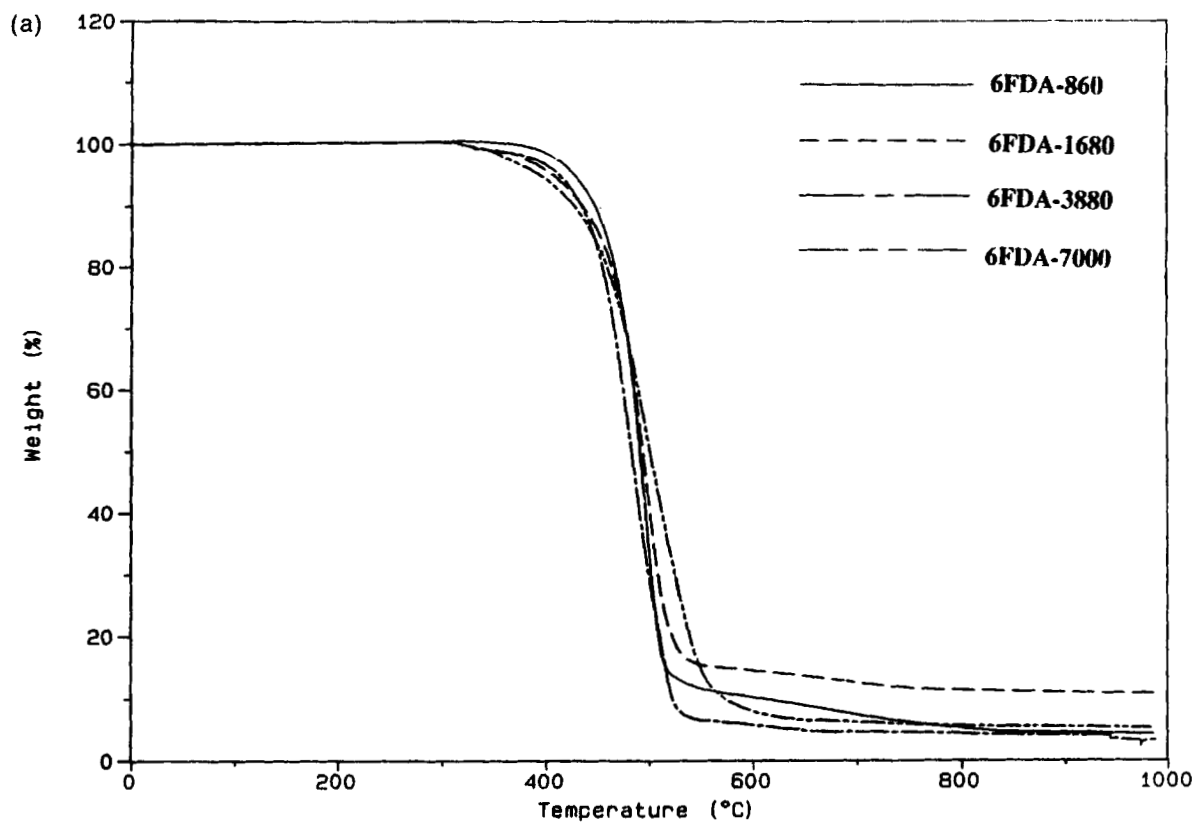[d] Yield of SPAA.

Figure 3   (a) TGA thermograms of poly(imide–siloxanes) from 6FDA–PDMS system. (b) TGA thermograms of poly(imide–siloxanes) from 6FDA–PDMS/860, BTDA–PDMS/860, and PMDA–PDMS/860 system.

graded compared to PMDA and BTDA. Sroog also reported that the structural variation of the above three dianhydrides resulted in differences in the thermal stability of the polyimides from p-phenylene diamine[21] and these three dianhydrides. The differences in thermal stability were similar to the result of this study.

Figure 4 shows typical decomposition profiles of PISIL from PMDA-860 measured by DTGA at four different heating rates (i.e., 2, 5, 10, and 20°C/min) in order to consider the relationship between degradation kinetics for heat resistance and the structural difference in the monomeric reactants. PISILs from BTDA-860 and 6FDA-860 show similar profiles. As can be seen in Figure 4, DTGA thermograms at different heating rates are parallel to one another and are superimposable on one another by shifting them along the abscissa.[22] Therefore, the thermal decomposition of the three PISILs was controlled by a single activation energy and further kinetic values can be obtained. If not superimposable during the thermal degradation reaction, this complex case would not be amenable to kinetic analysis.[13,22]

The activation energy at seven different decomposition fractions (i.e., 5, 7, 10, 15, 20, 30, and 40% as indicated in Fig. 4) was calculated from the slope of the straight lines used to fit the relationship between the logarithm of heating rates and $1000/T$ from PMDA-860 as shown in Figure 5. It was found that the activation energy increased with the percent weight loss or the conversion to degradation. PMDA-860 showed a slightly higher activation energy than that of BTDA-860. At a decomposition fraction of 10% for each tested sample, the activation energies of PMDA-860, BTDA-860, and 6FDA-860 were 181.4, 179.1, and 136.3 kJ/mol, respectively, as shown in Figure 6.

Based on the activation energy at a decomposition fraction of 10%, the preexponential factor (Z) can be calculated. The lifetime of the polyimides at different temperatures can be estimated from eq. (6) and are listed in Table II. For all three PISILs, k times $t_{1/2}$ over the decomposition temperature range was close to 0.693, indicating that the decomposition reaction followed first-order reaction kinetics (see Fig. 7).
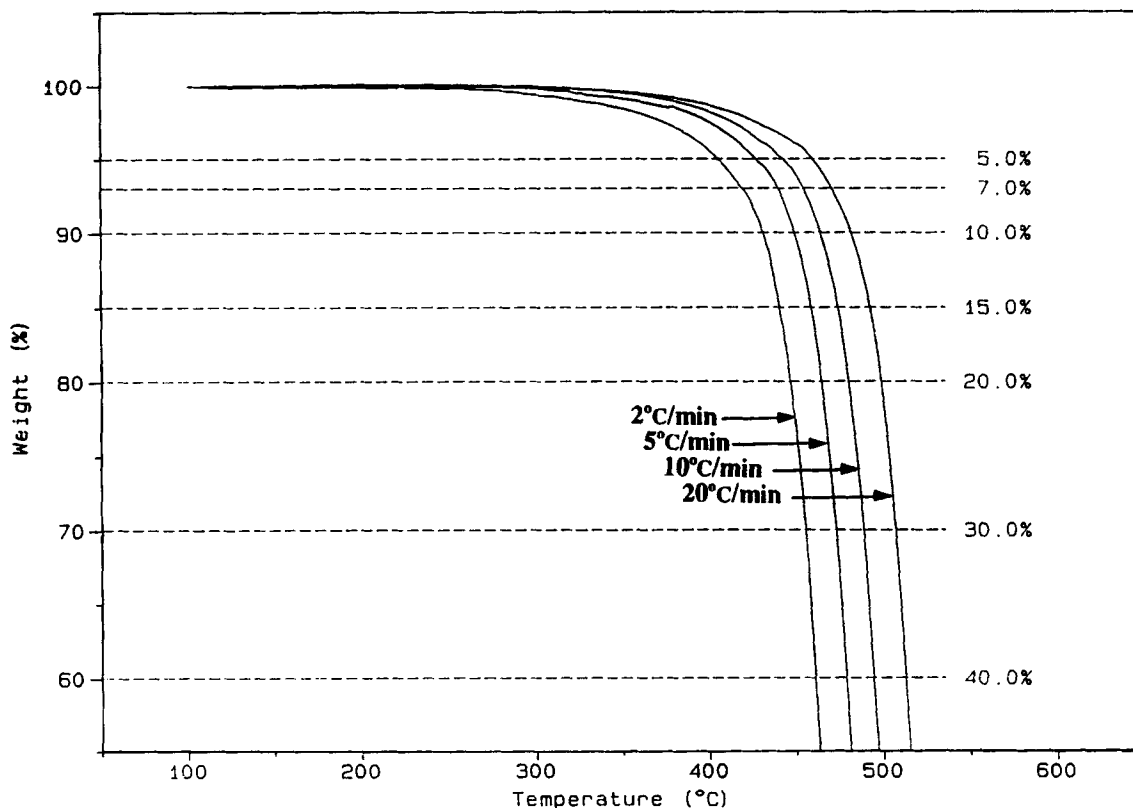

Figure 4   TGA thermograms of poly(imide–siloxane) from PMDA–PDMS/860 with the different heat rates: 2°C/min, 5°C/min, 10°C/min, and 20°C/min.
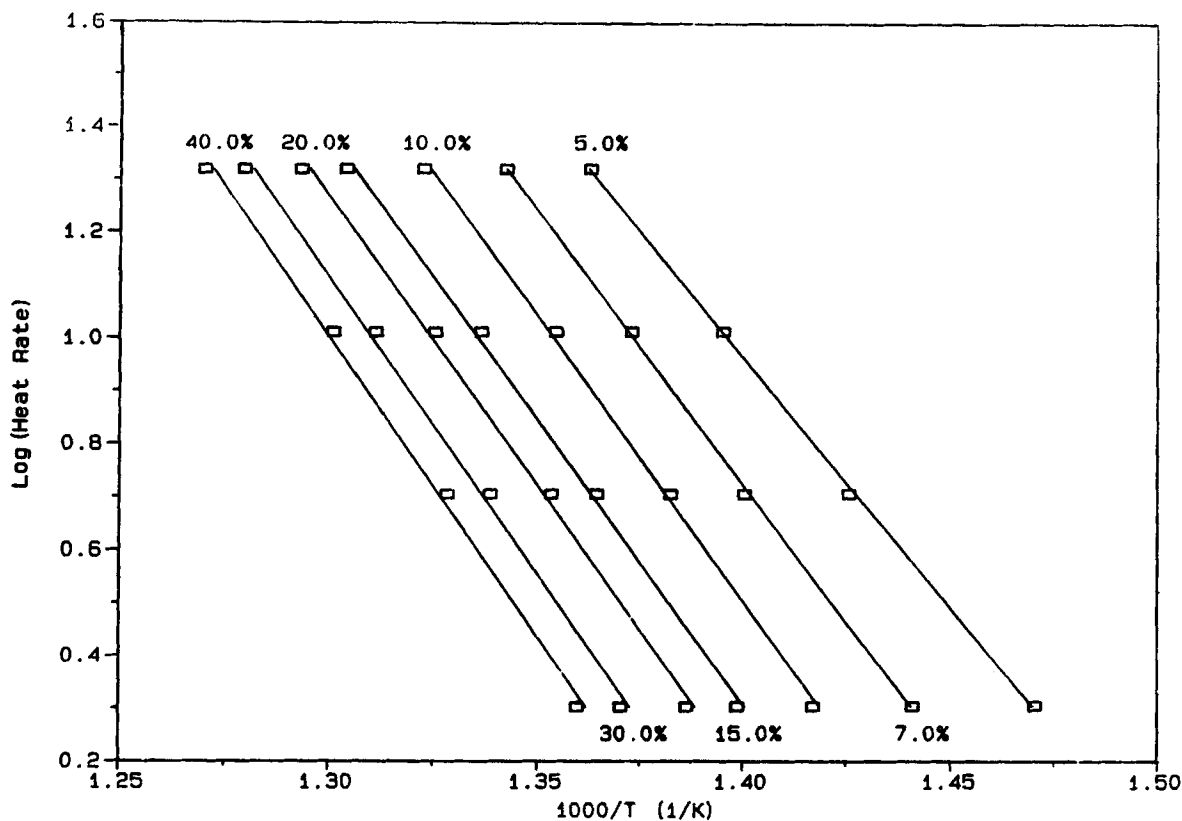
Figure 5 Relationship between T^{-1} and log β of poly(imide-siloxane) from PMDA-PDMS/860 at various conversion levels.

Figure 8 shows the predicted lifetime of PISILs at different temperatures. For example, under a nitrogen environment, PMDA-860 can last about 74 years (6.49×10^5 h) at a N_2 atmosphere of about 200°C. BTDA-860 can stand approximately 33 years

(3.33×10^5 h) of such exposure, but 6FDA-860 is less resistant than are BTDA-860 and PMDA in all the temperature ranges. In contrast, PMDA-860 lasts only a couple of days at about 350°C. From the
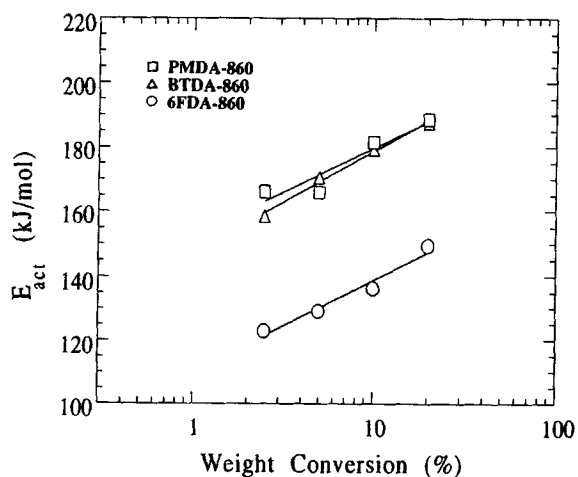

Figure 6 Changes of the thermal decomposition energy of poly(imide-siloxanes) under nitrogen flow.
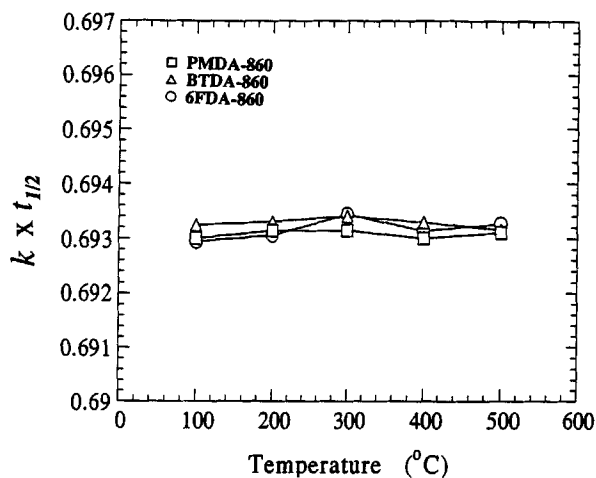

Figure 7 Dependence of $k \times t_{1/2}$ on the exposure temperature of poly(imide-siloxanes): (□) PMDA-860; (△) BTDA-860; (○) 6FDA-860.

Table II Rate Constants of First-order Degradation Reaction, k, and the Half-Lifetimes of Decomposed PISILs, $t_{1/2}$, Calculated from Eq. (6)

Temperature (°C)	PMDA-860		BTDA-860		6FDA-860	
	k	$t_{1/2}$	k	$t_{1/2}$	k	$t_{1/2}$
100	1.32E − 14	5.24E + 13	2.36E − 14	2.93E + 13	2.66E − 11	2.61E + 10
150	1.32E − 11	5.23E + 10	2.17E − 11	3.20E + 10	4.78E − 09	1.45E + 08
200	3.08E − 09	2.25E + 08	4.69E − 09	1.48E + 08	2.87E − 07	2.41E + 06
250	2.53E − 07	2.74E + 06	3.64E − 07	1.91E + 06	7.89E − 06	8.80E + 05
300	9.62E − 06	7.20E + 04	1.32E − 05	5.25E + 04	1.21E − 04	5.71E + 03
350	2.04E − 04	3.39E + 03	2.69E − 04	2.58E + 03	1.20E − 03	5.75E + 02
400	2.75E − 03	2.52E + 02	3.51E − 03	1.98E + 02	8.51E − 03	8.15E + 01
450	2.59E − 03	2.68E + 01	3.20E − 02	2.17E + 01	4.58E − 03	1.51E + 01
500	1.82E − 01	3.81E + 00	2.20E − 01	3.16E + 00	1.99E − 01	3.49E + 00

plot of the lifetime vs. the temperature, the thermal stability of PMDA-860 can be easily defined.

Comparison of Thermal Stability

Table III compares the thermal stability of various heat-resistant polymers with those of the present PISILs and lists other published activation energies for degradation of heat-resistant polymers.[7-12] Activation energy for decomposition at 10% weight loss was taken into account. The thermal stability of PMDA-860 is comparable to that of the commercial polyimide siloxane,[7] aromatic polyether I and II,[9] and poly(ether ether ketone),[10] respectively, and is
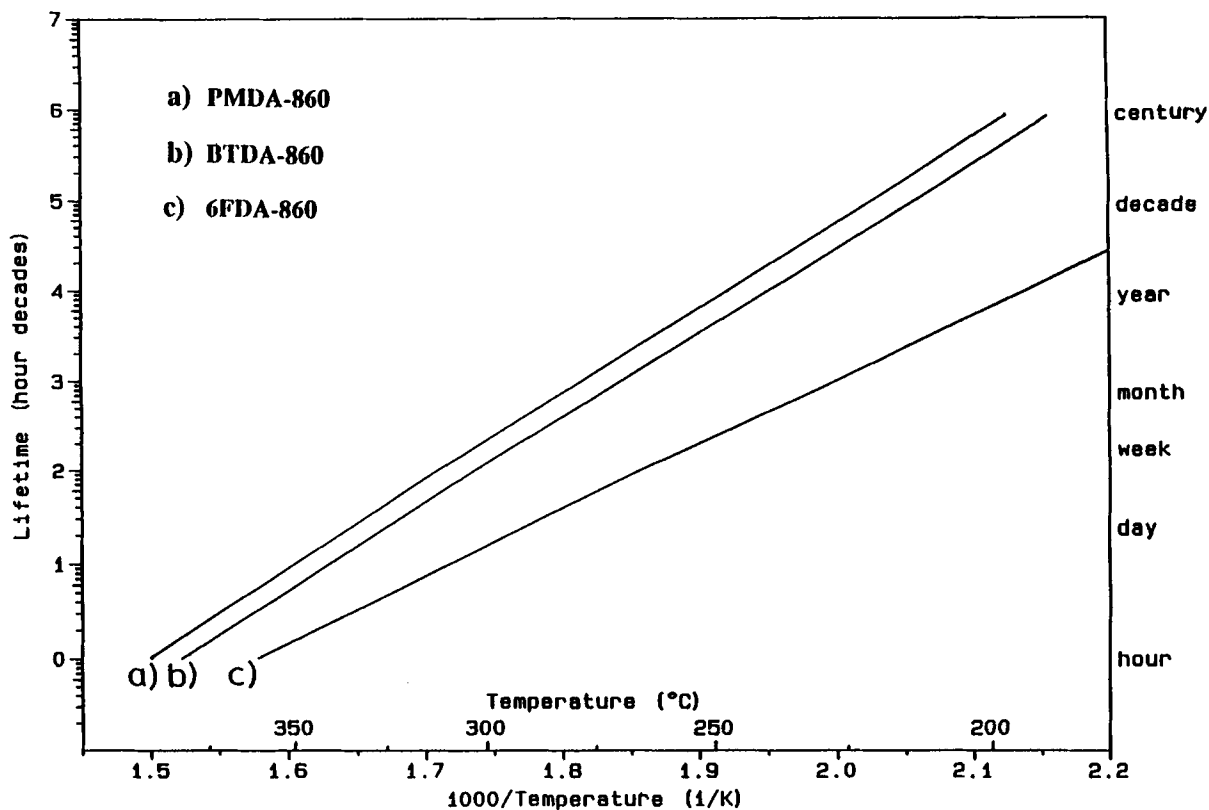

Figure 8 Estimated lifetime of three poly(imide–siloxanes) obtained from Ozawa's and Toop's methods at 10% conversion level.
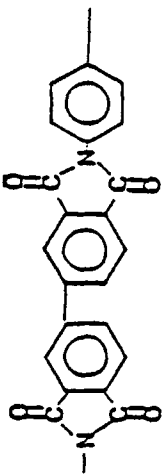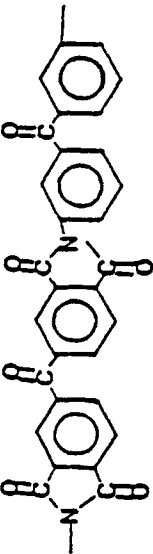
Table III Comparison of Thermal Stability of Various Kinds of Heat-resistant Polymers

Polymer Structure	Chemical Name	Activation Energy[a] (kJ/mol)	References
	Polyether I	164	9
	Polyether II	217	9
	Poly(ether ether ketone)	197	10
	Poly(imide–siloxane) (PMDA-860)	181	This study
	Poly(imide–siloxane) (BTDA-860)	179	This study

Table III (Continued)

	This study	
Poly(imide–siloxane) (6FDA-860)		136
Poly(ether imide)	10	219
Polysulfone	10	227
Poly(ether sulfone)	10	305
Poly(p-xylylene)	10	268
Polyimide (Kapton)	10	288
Polyimide (Upilex-R)	10	271

Table III (Continued)

Polymer Structure	Chemical Name	Activation Energy[a] (kJ/mol)	References
	Polyimide (Upilex-S)	316	10
	Polyimide (Larc-TPI)	248	10

[a] Calculated at degradation level (DL) of 10 wt %.

greater than that of the cured poly(butadiene–acrylonitrile–acrylic acid)[8] and Formvar.[13] However, the activation energy of PMDA-860 is much lower than that of the aromatic polyimides (see Table III). Particularly, PMDA-860 was more heat-resistant than were the aromatic poly(amide–imide) copolymers[23] from trimellitic anhydride (TMA) and 4,4'-methylene dianiline (MDA) or methylenediisocyanate (MDI) analyzed by its TGA thermogram (the temperature at 10% weight loss = 460°C). The activation energy of BTDA-860 at 10% weight loss was similar to that of phenolphthalein polycarbonate calculated by Pearce[22]—i.e., 179.1 and 178.5 kJ/mol, respectively.

CONCLUSION

PISILs were prepared from three aromatic dianhydrides (6FDA, BTDA, and PMDA) and PDMS diamines having different molecular weights. The fully cured PISILs were soluble in organic solvents, had subambient glass transition temperatures, and showed excellent thermal stability. The thermal stability and decomposition kinetics of PISILs were analyzed by DTGA decomposition kinetics. Among the 6FDA-based PISILs, the one having low molecular weight PDMS units in the backbone showed better thermal stability than that of the higher molecular weight PDMS. The thermal degradation path obeyed first-order kinetics where k times $t_{1/2}$ equals approximately 0.693. The activation energy of PISILs was in the following order: PMDA-860 > BTDA-860 > 6FDA-860. The activation energies at a decomposition fraction of 10% for PMDA-860, BTDA-860, and 6FDA-860 were 181.4, 179.1, and 136.3 kJ/mol, respectively. Among the PISILs, PMDA-860 showed the highest predicted lifetime. The thermal stability of PMDA-860 was comparable to that of aromatic polyethers. The activation energy of BTDA-860 and aromatic phenolphthalein polycarbonate had similar values at the decomposition conversion level of 10% weight loss.

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