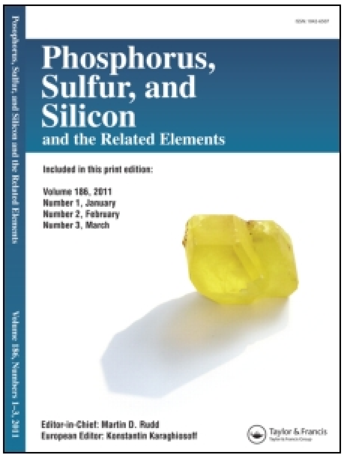

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THERMO-OXIDATIVE DEGRADATION OF THE POLYSILOXANEIMIDES DOPED WITH $LiCF_3SO_3$

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THERMO-OXIDATIVE DEGRADATION OF THE POLYSILOXANEIMIDES DOPED WITH $LiCF_3SO_3$

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The thermo-oxidative degradation of PSI-Li, lithium salt containing polysiloxaneimides, was studied by using thermal gravimetric analysis (TGA). Lithium salt reduces the decomposition temperatures of the siloxane sequences in PSI-Li complexes. From TGA data apparent activation energy E_a for degradation was evaluated following the method of Ozawa. The average activation energy $E_{a,av}$ in the 80% conversion of the lithium salt containing polyimide was lower than that of blank polyimide, whereas the $E_{a,av}$ of the lithium salt containing polysiloxaneimides were larger than that of polysiloxaneimides. The greater $E_{a,av}$ for PSI-Li may be rationalized on the basis of the formation of thermally stable structures.

Keywords: thermal gravimetric analysis; thermo-oxidative degradation; activation energy; lithium containing polysiloxaneimide

INTRODUCTION

Polysiloxaneimide (PSI) copolymers have been investigated by many research groups.[1,2] This class of materials has several advantages, such as low dielectric constant, superior adhesion, low moisture absorption, and ease of processing. Thermal stability of PSI copolymers has been studied.[3] Little work, however, has been reported on the apparent activation energy (E_a) of thermal degradation for PSI copolymers.[4] In a previous paper, we evaluated the apparent activation energies in thermo-oxidative degradation for PSI copolymers, and found that siloxane segments in PSI copolymers enhanced the thermo-oxidative stability.[5]

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Inorganic salts generally reduce the thermal stability of poly(propylene oxide) in an inert atmosphere but protect the polymer against thermal oxidation.[6] A similar effect is observed for poly(ethylene oxide).[7] On the other hand, metal-containing polyimides, prepared by adding inorganic salts or metal complexes have also been reported.[8] Taylor et al. reported the thermal stability of the lithium doped polyimide films, and found that the polymer decomposition temperature decreases.[9] In addition, Xu et al. found that the PSI doped with lithium trifluoromethanesulfonate ($LiCF_3SO_3$) can yield good conductivity properties.[10,11] However, thermal stability has not been reported on the PSI-Li complexes. To understand the effect of $LiCF_3SO_3$ on the degradation of PSI copolymers, we have measured their apparent activation energies for degradation in air. It is hoped that E_a will provided an insight into the effect of $LiCF_3SO_3$.

EXPERIMENTAL

Polymerization

The samples were the materials employed in our earlier work.[12] Yellow ocher solid PSI-Li complexes were prepared by cosolution of the $LiCF_3SO_3$ (TCI, Japan) and the PSI in dry N,N′-dimethylacetamide, as shown in Scheme 1. Complexes are designed so that, for example, PSI-1300(10)-Li denotes a complex of PSI-1300(10) with $LiCF_3SO_3$ in which PSI copolymer containing 10 wt % of siloxane that number-average molecular weight is 1300 g/mol.

Characterization

Differential scanning calorimetry (DSC) was used to determine the glass transition temperature (T_g) with a Dupont 910 DSC, at a heating rate of 10°C/min. The characteristics and kinetics of degradation of polymers were measured by Seiko SSC 5000 TG/DTA instrument. Heating rates (B) of 5, 10, 20, and 40°C/min were used. The sample weight was about 10 mg, and the air flow rate was kept at 100 mL/min.

RESULTS AND DISCUSSION

Thermal property

The glass transition temperatures T_g's of samples determined by DSC are listed in Table I. The T_g's of complexes are larger than that of blank polymers. These imply that the additive influences regularity of structure.

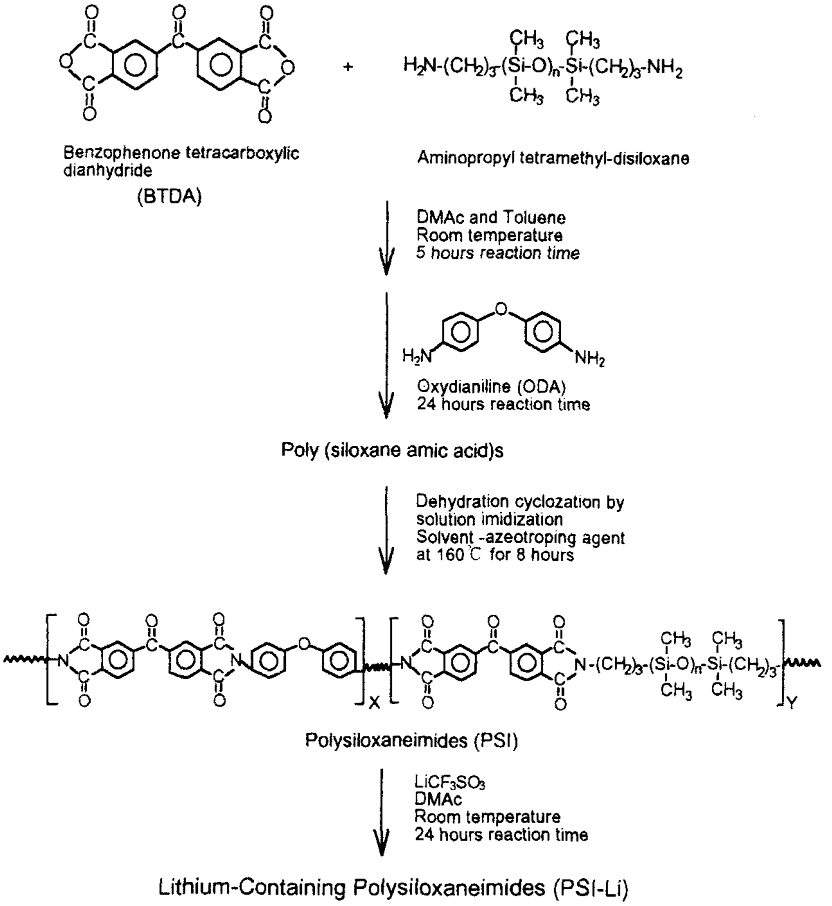

Figure 1 shows the TGA curves in air of the representative lithium salt containing polymers and their blank polymers. Clearly, introducing lithium salt into the polymers produce some decrease in decomposition temperature. PSI-1300(20)-Li complex starts to lose weight around 290°C and its thermal degradation shows two stages of weight loss. The former is subjected to the decomposition of siloxane, and the latter is due to the degradation of ODA.[13] A similar trend is also observed for the other PSI-Li complexes. Qualitative characterization of the degradation process is illustrated by the 5% weight loss temperature and the maximum rate temperatures of weight loss, T_5 and T_m. Table I show the characteristic temperatures of degradation in air for complexes. Comparing the T_5 and T_m of these complexes with blank polymers, the complexes are less stable than the blank polymers. Furthermore, the T_5 is decreased as the

TABLE I Characteristic temperatures on TGA curves at 10°C/min heating rate under air atmosphere.

polymer	T_g^a (°C)	T_5^b (°C)	T_{1m}^c (°C)	T_{2m} (°C)	Y_c^d (wt%)
PI-Li	276 (259)[e]	440 (483)	—	603 (610)	1.5 (0.0)
PSI- 276 (20)-Li	165 (155)	320 (422)	437 (485)	600 (606)	7.0 (5.0)
PSI-1300 (10)-Li	276 (253)	283 (414)	440 (482)	572 (604)	4.0 (2.5)
PSI-1300 (20)-Li	246 (241)	340 (402)	430 (443)	590 (625)	7.2 (6.0)
PSI-1300 (30)-Li	250 (236)	220 (394)	426 (435)	607 (635)	9.3 (8.8)
PSI-4400 (20)-Li	275 (254)	370 (397)	453 (473)	602 (615)	5.7 (5.3)

[a] T_g (glass transition temperature) were determined by DSC in N_2 at a heating rate of 10°C/min.
[b] A 5% weight loss temperature observed in TGA.
[c] The temperature at which maximum rate of weight loss occurs at the first and second step, T_{1m} and T_{2m}.
[d] Y_c = Char residue at 800°C
[e] Number in parentheses indicate the value of PI or PSI polymers.

siloxane segment molecular weight is decreased and the concentration of n-propyl linkages in the PSI-1300-Li complex increases. Thus, the existence of the lithium salt promotes the decomposition of the aliphatic n-propyl segments linking the siloxane segments to the polyimide matrix. The maximum rate of weight loss temperature in first step T_{1m} decreases with increasing in siloxane content for PSI-1300-Li complex, whereas that in secondary step T_{2m} increases. The results reveal that the decomposition of the polyimide segments is affected by the decomposition products from siloxane segments. On the other hand, char yield Y_c in degradation of PSI-1300-Li is proportional to the siloxane content (Table I), and Y_c of the complexes are larger than that of the blank polymers. This may be associated with the Li_2O generated during thermo-oxidative degradation.[9]

Kinetic analysis

The method of calculation of apparent activation energy E_a for the polymer degradation, proposed by Ozawa[14], requires several TGA curves at different heating rates (B). A representative result is shown in Figure 2. The relationships of the logarithm of the heating rate (log B) vs $1/T$ for each value of α (α = weight loss at a given temperature/total weight loss of the degradation) show excellent linearity. From the isoconversion curve, apparent activation energies are calculated from the slopes of the lines using the expression

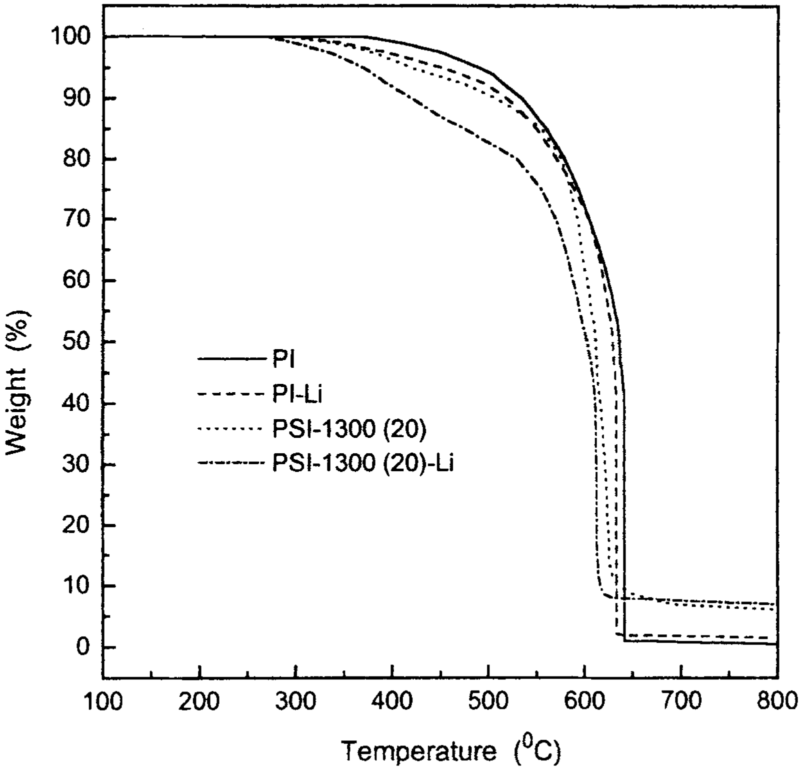

FIGURE 1 TGA thermograms of polymers PI, PI-Li, PSI-1300(20) and PSI-1300(20)-Li in air at the heating rate 10°C/min.

$$E_a = -\mathit{slope} \times R/0.457$$

where R is the gas constant. The apparent activation energies and their average values for the range of conversion 10% to 80% ($E_{a,av} = \sum_{\alpha=0.1}^{0.8} E_{a,\alpha}/8$) of the samples are listed in Table II.

The activation energies of the samples show a large variation with the degree of conversion that is expected due to the continuous change of degradation mechanism. It is interesting that $E_{a,av}$ of the degradation of the PSI-Li complexes in air are larger than that for blank PSI copolymers. In contrast, $E_{a,av}$ of the degradation of the PI-Li complex is lower than that for blank PI polymer (Table II). The likely explanation is that the degradation products of the PSI-Li complexes have a retarding effect on chain scission of imide segments.

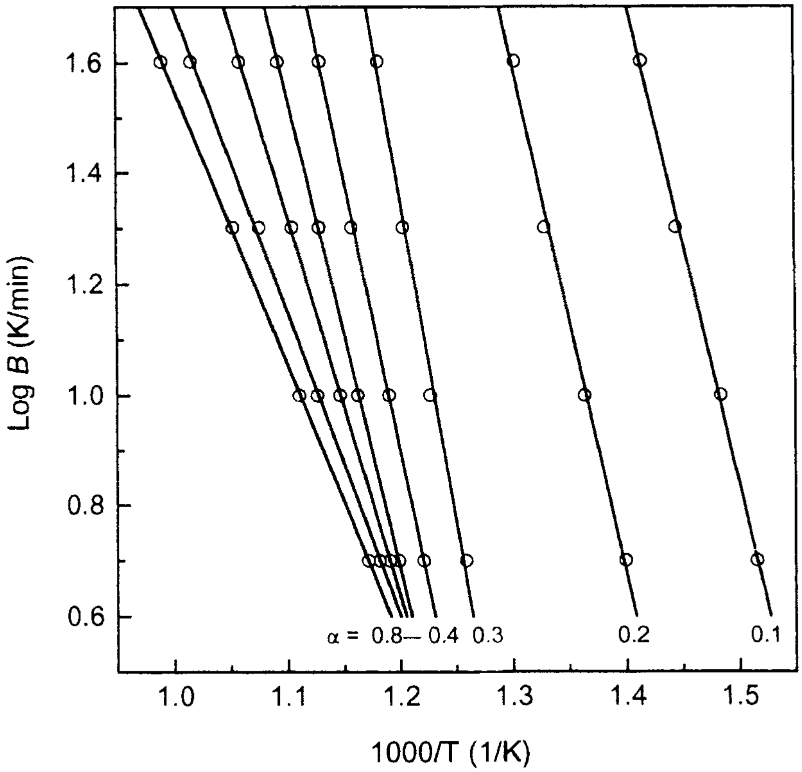

FIGURE 2 The dependence of logarithm of heating rate (log B) vs. reciprocal absolute temperature ($1/T$) for the Ozawa method at indicated conversions (α) of decomposition of PSI-1300(30)-Li in air.

TABLE II Activation energies E_a (kJ/mol) in air of the complexes degradation process calculated by Ozawa method.

polymer	*Conversion(α)*								$E_{a,av}{}^{a}$
	0.1	*0.2*	*0.3*	*0.4*	*0.5*	*0.6*	*0.7*	*0.8*	
PI-Li	169	166	163	171	189	252	239	200	194 (208)
PSI-276 (20)-Li	113	139	224	206	166	149	134	119	156 (122)
PSI-1300 (10)-Li	134	151	172	175	186	186	156	111	159 (123)
PSI-1300 (20)-Li	155	184	172	189	183	166	138	108	162 (136)
PSI-1300 (30)-Li	158	174	216	231	187	158	123	110	170 (161)
PSI-4400 (20)-Li	189	230	193	187	195	189	172	140	187 (142)

[a] Average activation energy of conversion (0.1 ≤ α ≤ 0.8) in air. Number in parentheses indicate the value of PI or PSI polymers.

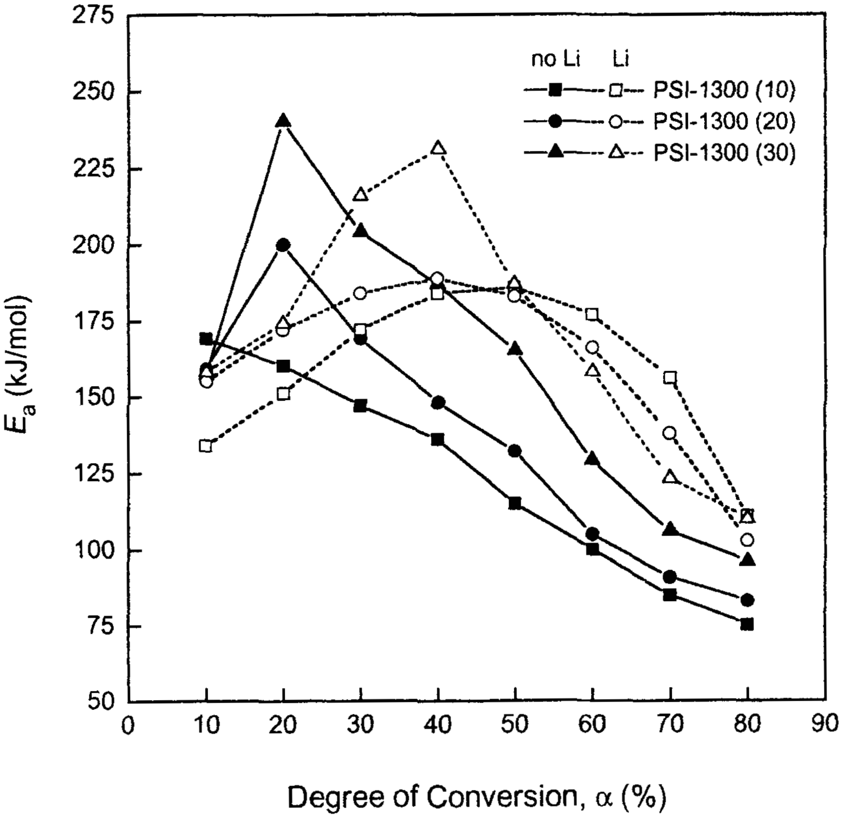

FIGURE 3 The effect of siloxane content on E_a of degradation for PSI-1300 copolymers and their complexes.

The values of $E_{a,av}$ for PSI-Li complexes increase with increase chain length of the siloxane segments, as listed in Table II. On the other hand, the effect of siloxane content on the activation energies of PSI-Li complexes is shown in Figure 3. It is found that E_a for the degradation of the PSI-1300-Li complexes increase with increasing conversion in the range of $0.10 \leq \alpha \leq 0.40$ and decrease in the range of $0.50 \leq \alpha \leq 0.80$. Moreover, the average activation energy for thermo-oxidative degradation increases with increasing siloxane content. The greater $E_{a,av}$ for PSI-1300(30)-Li may be rationalized on the basis of the formation of thermally stable structures. It is may be associated with the oxidative crosslinking through the methyl groups that have been reported for polydimethylsiloxane.[15]

The existence of the lithium salt promotes the decomposition of the PSI copolymers. However, the average activation energies $E_{a,av}$ of thermo-oxidative degradation of the PSI-Li complexes are larger than that for blank PSI copolymers. Moreover, the values of $E_{a,av}$ for PSI-Li complexes increase with increasing chain length and content of siloxane segments.

Acknowledgements

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