

Macromolecular Research

Volume 12, Number 6 December 31, 2004

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Hydrolytic Stability of Sulfonic Acid-Containing Polyimides for Fuel Cell Membranes

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Received March 10, 2004; Revised November 12, 2004

Abstract: The long-term stability of sulfonic acid-containing polyimides has been investigated. The hydrolytic degradation of homopolyimide and the block copolyimide comprising 27 mol% of 2,2'-bis(trifluoromethyl)benzidine and 9 mol% of *m*-phenylenediamine (BTFMB27mP10[7/(3+1)]), was quantified through viscosity measurements and FT-IR spectroscopic analyses. The viscosity decrease with respect to time and the degradation rate were similar. The degrees of degradation with respect to time under ambient conditions and at elevated temperature in water were monitored by FT-IR spectroscopy. A new absorption peak was observed at 1786 cm⁻¹, which corresponds to the presence of anhydride end groups formed by hydrolytic scission of the imide rings.

Keywords: anhydride, FT-IR spectroscopy, hydrolytic degradation, polyimides, sulfonic acid, viscosity.

Introduction

We have been developing novel water insoluble proton conducting rigid rod sulfonic acid containing polyimides that have good mechanical properties.¹ Copolyimides containing bulky or angled comonomer had the same or higher conductivities at all relative humidity ranges than Nafion®.²

It was shown that a small fraction of the comonomer generated nanoscale pores lined with sulfonic acid groups. Such pores absorb water strongly even at relatively low humidity. However, these copolyimides either dissolved or fragmented easily in water at elevated temperatures.

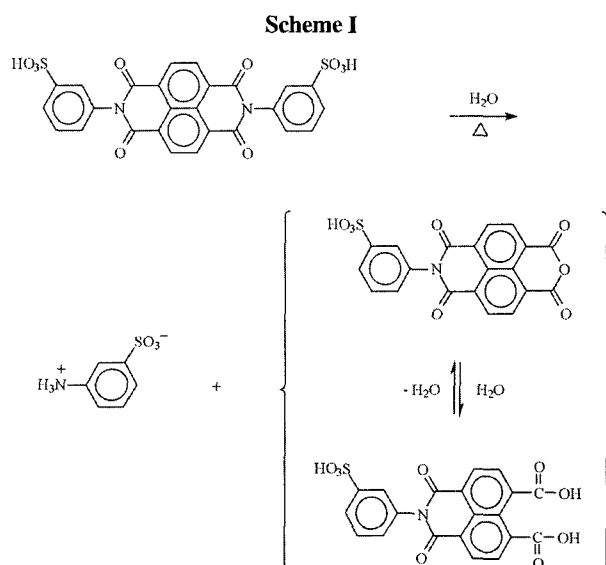
2,2'-Bis(trifluoromethyl)benzidine (TFMB) was used as a comonomer in this research to prevent water solubility. *m*-Phenylenediamine (*m*-PDA), an angled comonomer, was introduced to compensate for the conductivity loss due to the hydrophobicity of TFMB. Copolyimides with different

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combinations of TFMB and *m*-PDA were synthesized in order to study the relationships between conductivity and water insolubility.³ BTFMB27mP9[7/(3+1)] (B signifies a block copolymer and the numbers indicate molar fraction of the comonomers out of 100, so this polymer has 27 mole% of TFMB and 9 mole% of *m*-PDA; 7 indicates 7 unit block of 4,4'-diamino-2,2'-biphenyldisulfonic acid (DAPS) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), and 3+1 indicates a block consisting of mixture of 3 parts of TFMB and 1 part of *m*-PDA with NTDA). This polymer had reasonable conductivity, and was not soluble in water at 90 °C.

Many polymers tend to hydrolyze with environmental exposure. Sroog *et al.* reported the effect of water on the mechanical properties of polyimides.⁴ 5-Membered ring polyimide films were placed in boiling water and the decrease of mechanical strength of the films as a function of time was investigated. Also, Deiasi *et al.*⁵ prepared several different kinds of 5-membered ring polyimides. The polyimide films were immersed in water at different temperatures, and the decrease of mechanical properties was measured. They reported that the decrease of mechanical strength was accelerated in alkaline (pH > 12) or acidic (pH < 2) media.

Long-term stability of sulfonated polyimides is necessary if they are to be used as proton exchange membranes (PEMs) in a fuel cell. Faure, Mercier, Pineri *et al.*⁶ demonstrated that the sulfonated polymer membrane could be used for PEMs. Especially, sulfonated 6-membered ring polyimide membranes were stable more than 2,000 hrs at 60 °C. Recently, they prepared model compounds, and investigated the effect of sulfonic acid on the hydrolytic scission of imide group of the compounds.⁷ The model compound was placed in water at 80 °C for 120 hrs, and the degraded compound was analyzed using NMR. They concluded that 6-membered



imide ring hydrolyzed to the mixture of anhydride and diacid (Scheme I). Even though the research was quite systematic for the model compound, studies on the sulfonic acid containing polyimides were not described.

We observed that the mechanical properties of our sulfonic acid containing polyimides slowly degraded under ambient conditions. It was decided to systematically study the degradation under ambient conditions, and also at elevated temperature in water by viscosity measurement and FT-IR analysis. The results of this study are presented below.

Experimental

Polyimide Preparation. Homopolyimide and copolyimide (BTFMB27mP9[7/(3+1)]) were synthesized and their cast

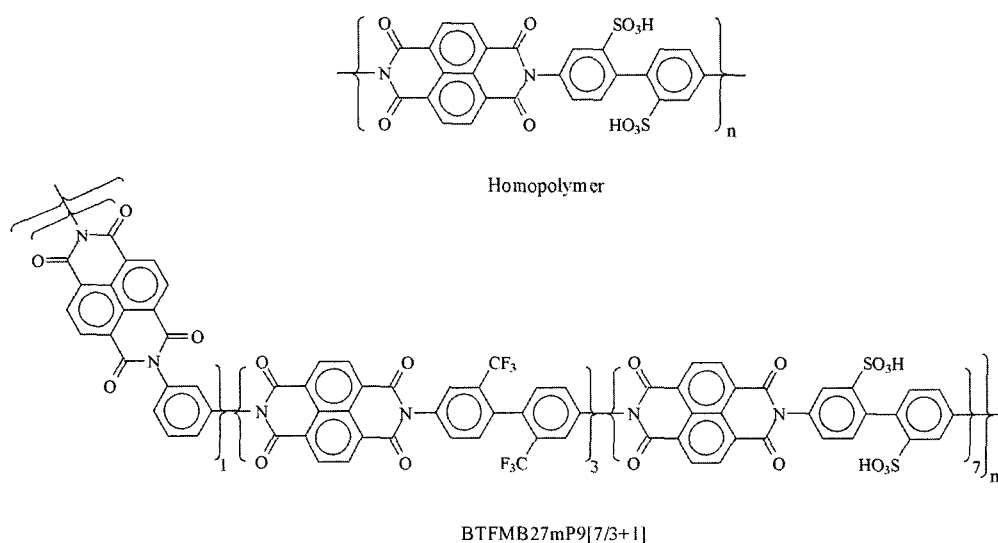


Figure 1. Structures of homopolyimide and BTFMB27mP9[7/(3+1)].

films were prepared using the methods described earlier.³ Their structures are presented in Figure 1.

Viscosity Measurements. Homopolymer and BTFMB 27mP9[7/(3+1)] fibers were kept in the laboratory under ambient conditions. A sample was taken every few months. It was dried under vacuum (0.1 mmHg) at 80 °C for 36 hrs. Different weights of polymer were placed in 25 mL volumetric flasks and dissolved in DMSO; solution viscosities were measured using an Ubbelohde viscometer in a water bath at 30 °C.

FT-IR Analysis. Several small pieces of copolymer film (0.5 × 0.5 cm²) were placed in 90 °C DI water in a round bottom flask equipped with a condenser and a thermometer. Pieces were taken at intervals of 5 to 40 days, washed with methanol and dried. They were dissolved in DMSO; the solution was cast on a KBr plate and dried under vacuum (0.1 mmHg) at 80 °C for 30 hrs before running transmission Fourier transform infrared (FT-IR) spectra. FT-IR spectra were obtained on a Bomem Michelson MB110 FT-IR spectrophotometer that was equipped with a liquid nitrogen cooled, mercury-cadmium-telluride (MCT) detector.

Preparation of Triisobutylamine (5%) and Zn Salts (20%) of BTFMB27mP9[7/(3+1)]. BTFMB27mP9[7/(3+1)] was dried under vacuum (0.1 mmHg) at 80 °C for 36 hrs. A portion was weighed (0.83 g, 1.51 mmol) and dissolved in 16 mL of DMSO. A DMSO solution (2 mL) of triisobutylamine (TIBA) (0.018 g, 0.10 mmol) was added to the DMSO solution of the BTFMB27mP9[7/(3+1)]. Five percent of the copolyimide acid groups were reacted with TIBA. Also, Zn(OAc)₂ · 2H₂O (0.098 g, 0.44 mmol) was added to a DMSO solution (20 mL) of BTFMB27mP9[7/(3+1)] (0.95 g, 1.73 mmol). Twenty percent of the copolyimide acid groups were neutralized.

The solution of the partially neutralized copolymer was poured on a glass plate. The thickness of the solution on the glass was controlled using an adjustable doctor blade. It was placed in an oven equipped with a thermometer, and DMSO was removed under reduced pressure (0.1 mmHg) at room temperature for 30 min. Oven temperature increased to 80 °C over 30 min under the same pressure. Residual DMSO was removed by heating it under vacuum at 80 °C for 30 hrs. The film was detached from the glass plate and soaked in methanol for 24 hrs to remove traces of DMSO in the film. It was then dried under vacuum at room temperature.

Results and Discussion

Viscosity. Two batches each of homopolyimide and BTFMB27mP9[7/(3+1)] fibers were kept under ambient laboratory conditions. Samples were taken every few months, and viscosities were measured. Solution viscosity is basically a measure of polymer molecular weight. Figure 2 shows a typical viscosity vs. concentration plot of freshly prepared homopolyimide. The extrapolation of reduced viscosity and

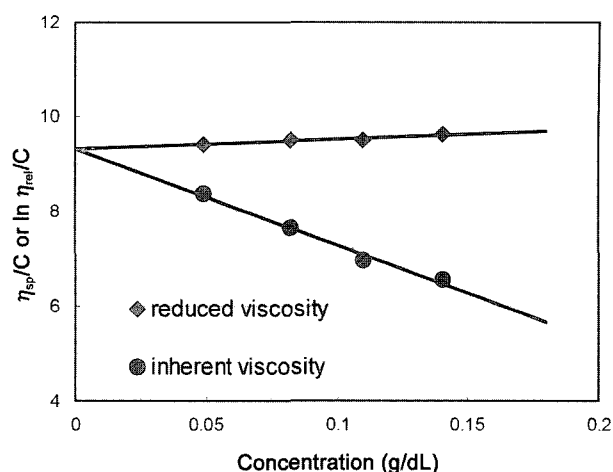


Figure 2. Intrinsic viscosity ($[\eta] = 9.3$ dL/g) measurement of homopolyimide, batch iv8.

inherent viscosity to zero concentration gives intrinsic viscosity, $[\eta]$.

For most linear polymers, the relation between $[\eta]$ and molecular weight can be expressed simply in the Mark-Houwink equation.⁸

$$[\eta] = K' M^a \quad (1)$$

where K' and a are constants and functions of the solvent as well as of the polymer type. So, molecular weight decrease by degradation can be analyzed by the viscosity measurement if a is near 1. For rigid rod polymers, it is usually between 1 and 1.5.⁹

The relationship between the number of repeat units in a polymer (N) and time (t) for random chain scission can be expressed as¹⁰:

$$(1/N_t) - (1/N_0) = kt \quad (2)$$

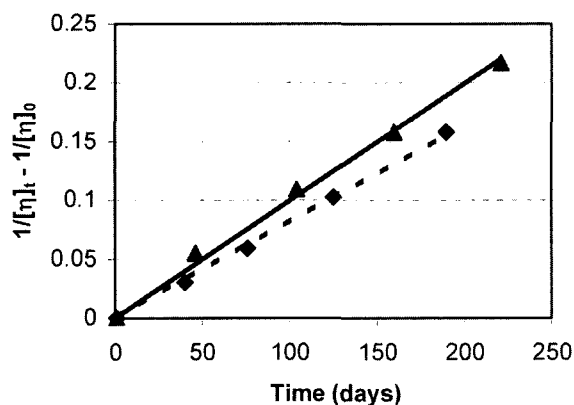
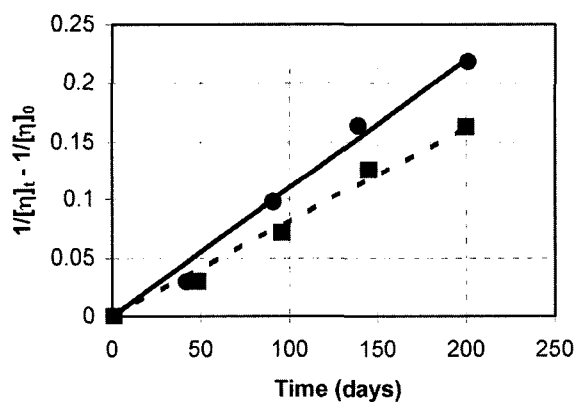
where N_0 and N_t are the number of repeat units of the polymer at time zero and t , and k is a rate constant for the chain scission. For our sulfonic acid containing polyimides, we do not have an absolute value for the N . Therefore, we used $[\eta]$ which is approximately proportional to N .

Plots of $(1/[\eta]_t - 1/[\eta]_0)$ ($[\eta]_0$ and $[\eta]_t$ are the intrinsic viscosities of the polymer at time zero and t) vs. time (days) for these polymers are presented in Figures 3 and 4. Slopes and standard deviations from the plots are listed in Table I. The slopes correlate with the degradation rates of the polymers.

There were no large differences in degradation rates between the homopolymer and BTFMB27mP9[7/(3+1)], even though the copolyimide had only 64% of the sulfonic acid groups of the homopolymer. In a previous study,³ BTFMB27mP9[7/(3+1)] was found to have more water molecules per sulfonic acid group than the homopolymer under ambient conditions. The extra water in the copolyimide

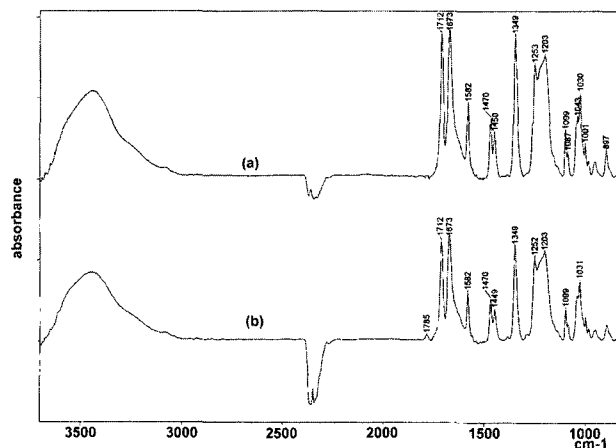
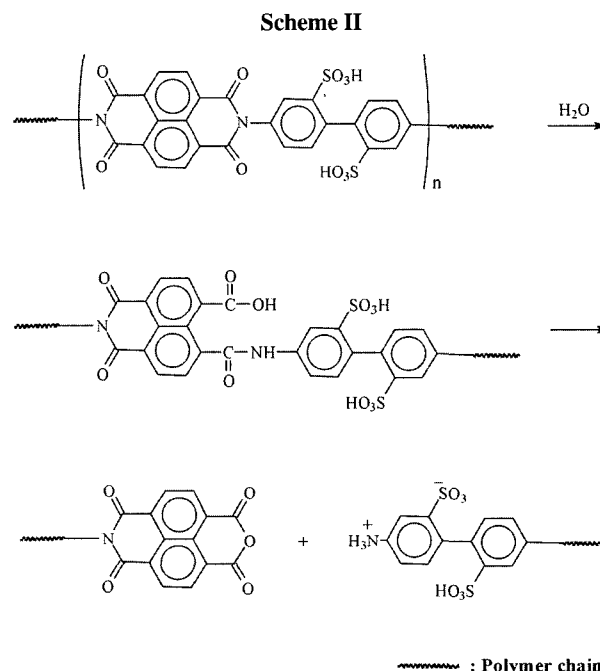
Table I. Slopes and Standard Deviations of Plots of $(1/[\eta]_t - 1/[\eta]_0)$ vs. Time for Polyimides

Polyimide	$[\eta]_0$ dL/g	$[\eta]$ (days) dL/g	Slope(/day)	Standard Deviation of Slope
Homopolymer (batch iv0)	7.1	2.8 (220 days)	9.7E-4	3.1E-5
Homopolymer (batch iv8)	9.3	3.8 (190 days)	8.4E-4	1.6E-5
BTFMB27mP9[7/3+1] (batch iv15)	4.4	2.3 (200 days)	11.4E-4	6.7E-5
BTFMB27mP9[7/3+1] (batch iv9)	6.3	3.1 (200 days)	8.5E-4	4.3E-5

**Figure 3.** Plot of $(1/[\eta]_t - 1/[\eta]_0)$ vs. time for homopolyimide (solid line: batch iv0; dotted line: batch iv8).**Figure 4.** Plot of $(1/[\eta]_t - 1/[\eta]_0)$ vs. time for BTFMB27mP9[7/(3+1)] (solid line: batch iv15; dotted line: batch iv9).

could accelerate the degradation. This might be the reason that the homopolymer and BTFMB27mP9[7/(3+1)] had similar degradation rates.

FT-IR Analysis. FT-IR spectra of fresh and one year old homopolyimide under ambient conditions are shown in Figure 5. The spectrum of the one year old homopolymer shows a small peak at 1785 cm^{-1} that does not appear in the spectrum of the fresh homopolymer. The peak corresponds to anhydride end carbonyl groups of degraded polyimide. Proposed structures for the degradation are presented in Scheme II.

**Figure 5.** FT-IR spectra of (a) fresh and (b) one year old homopolyimide batch iv8.

There are several reasons for proposing that the peak at 1785 cm^{-1} is due to anhydride end groups. The C=O stretching band for anhydride groups of 1,4,5,8-naphthalenetetracarboxylic dianhydride appears at 1780 cm^{-1} .¹¹ According to our viscosity measurements, there was severe degradation;

the viscosity of homopolymer dropped from 9.3 to 3.8 dL/g in 190 days. The viscosity drop implies chain cleavage, rather than just hydrolysis to the amic acid. Genies and Mercier *et al.*⁷ found that sulfonic acid containing model compound decomposed in 80°C water and formed an equilibrium between anhydride and diacid (Scheme I). The C=O stretching band for the -CO₂H groups of 1,4,5,8-naphthalenetetracarboxylic acid appears at 1720-1727 cm⁻¹.¹¹ It would be hidden under the strong peak at 1712 cm⁻¹ and would not be visible. However, because this hydrolysis occurred with very little water present, most of the ends were probably in the anhydride form.

The extent of hydrolysis of the homopolymer was analyzed with time. FT-IR spectra of fresh, 190 day old and one year old homopolymer were obtained. They are shown in Figure 6. The peak at 1582 cm⁻¹, which is assigned to the aromatic C-C stretch, was used as a reference, and the spectra were normalized with respect to it. The carbonyl peaks could then be compared. The peak at 1785 cm⁻¹ increased with time. The imide peaks at 1712 and 1673 cm⁻¹ decreased with time, confirming its hydrolysis.

Based on the FT-IR spectra in Figure 6, a plot of the ratio of imide peak (A_t/A_0 , A_0 and A_t are peak heights at 1673 cm⁻¹ at time zero and t) vs. time (days) for the homopolymer is shown in Figure 7. It shows 9% hydrolytic scission of the imide group in one year. A plot of the ratio of anhydride peak at 1785 cm⁻¹ to aromatic C-C stretch peak at 1582 cm⁻¹ vs. time (days) for the homopolymer is shown in Figure 8. The degradation was linear with time.

We can obtain the ratio (N_t/N_0) of the number of polymer molecules at time t to 0 from the viscosity measurements (Figure 8 and Table I). For our polymer, the relation between $[\eta]$ and degree of polymerization (X_n) can be expressed very approximately as

$$[\eta] = KX_n^{-1} \quad (3)$$

where K is a constant. N_t/N_0 using is then obtained the following equation:

$$N_t/N_0 = [\eta]_0/[\eta]_t = (X_{n0})/(X_{nt}) = 1 + [\eta]_0 kt \quad (4)$$

where $[\eta]_0$ and $[\eta]_t$ are the intrinsic viscosities of the polymer at time zero and t (for example, $[\eta]_0 = 9.3$, $[\eta]_{1\text{year}} = 2.0$ (extrapolated value) for homopolymer batch iv8), and k is a rate constant for the chain scission. Also, we can obtain N_t/N_0 from the FT-IR analysis (Figure 7) and Eq. (5):

$$N_t/N_0 = 1 + C_t X_{n0} \quad (5)$$

where C_t is cleavage rate in one polymer molecule at time t ($C_{1\text{year}} \approx 0.09$ from Figure 7).

The ratios (N_t/N_0) of the number of polymer molecules at time t to 0 measured by both the viscosity measurements

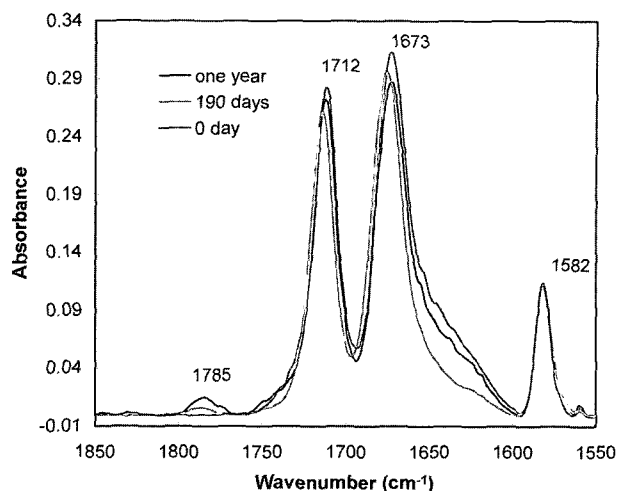


Figure 6. FT-IR spectra of fresh, 190 day old and one year old homopolymer (batch iv8), normalized to the aromatic C-C stretch peak at 1582 cm⁻¹.

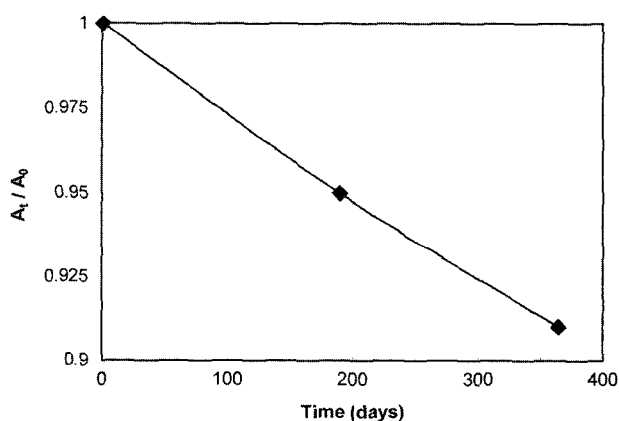


Figure 7. Plot of absorbance ratio, A_t/A_0 , vs. time for the homopolymer (A_0 and A_t are peak heights at 1673 cm⁻¹ at time zero and t from FT-IR spectra in Figure 6).

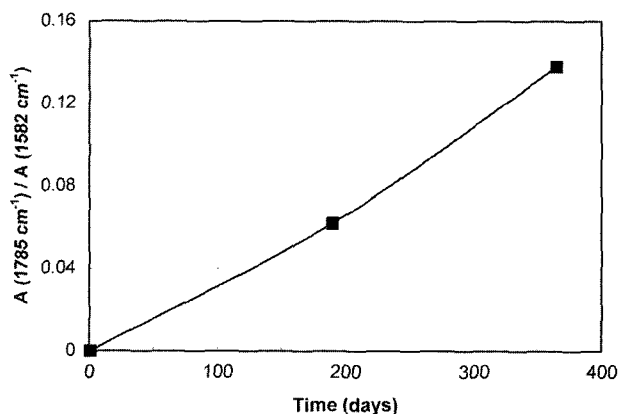


Figure 8. Plot of absorbance ratio, $A(1785 \text{ cm}^{-1})/A(1582 \text{ cm}^{-1})$, vs. time for homopolymer.

and FT-IR analyses should be identical. Therefore, we have the equation:

$$[\eta]_0/[\eta]_t = 1 + C_t X_{n0} \quad (6)$$

Using Eq. (6), we can find an approximate value for the initial degree of polymerization (homopolymer (batch iv8): $X_{n0} \approx 40$; BTFMB27mP9[7/(3+1)] (batch iv9): $[\eta]_0 = 6.3$, $[\eta]_{200\text{days}} = 3.1$, $C_{200\text{days}} = 0.04$, $X_{n0} \approx 26$).

The triisobutylamine (TIBA) salt of BTFMB27mP9[7/(3+1)] was prepared to determine if lowering the acidity would slow the hydrolytic scission of imide group. BTFMB27mP9[7/(3+1)] and its 5% TIBA salt were placed separately in 90°C DI water for 25 days. They were analyzed using FT-IR. Both show a similar size peak at 1786 cm^{-1} .

The 20% Zn salt of BTFMB27mP9[7/(3+1)] was also synthesized and compared with BTFMB27mP9[7/(3+1)]. They were placed separately in 90°C DI water and monitored using FT-IR. FT-IR spectra of BTFMB27mP9[7/(3+1)] were obtained after 20 and 40 days, and compared with its fresh FT-IR spectrum. The results are shown in Figure 9. The peak at 1582 cm^{-1} , assigned to the aromatic C-C stretch, was used as a reference, and the spectra were normalized with respect to it. The carbonyl peaks could then be compared. The peak at 1786 cm^{-1} increased with time. The imide peaks at 1714 and 1676 cm^{-1} decreased with time, confirming its hydrolysis.

The FT-IR spectra of the 20% Zn salt of BTFMB27mP9[7/(3+1)] were obtained after 5, 10 and 40 days, and compared with that of the fresh copolymer (Figure 10). They showed the same pattern as BTFMB27mP9[7/(3+1)]. The peak at 1786 cm^{-1} increased and peaks at 1714 and 1676 cm^{-1} decreased with time.

We expected that if the salt of the copolyimide had a lower hydrolytic scission rate than the acid form; the effect should be observable in the FT-IR spectra. However, quantitative analysis was not easy. The anhydride peak is very small, especially in the early stages (2 to 4 days).

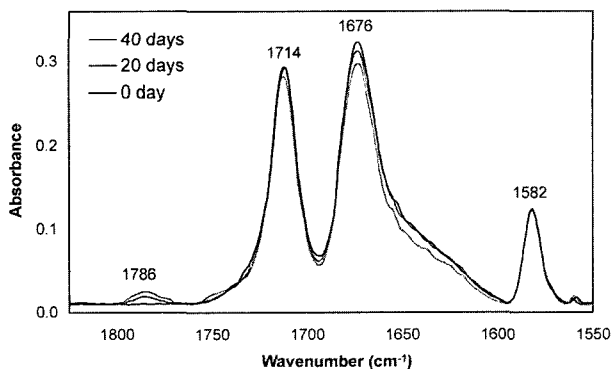


Figure 9. FT-IR spectra of BTFMB27mP9[7/3+1] (batch iv9) after 0, 20 and 40 days in 90°C water, normalized to the aromatic C-C stretch peak at 1582 cm^{-1} .

Based on the FT-IR spectra (Figures 9 and 10), plots of the ratio of imide peak (A_t/A_0 , A_0 and A_t are peak heights at time zero and t ; 1676 cm^{-1} for BTFMB27mP9[7/(3+1)]; 1714 cm^{-1} for 20% Zn salt BTFMB27mP9[7/(3+1)]) vs. time (days) for BTFMB27mP9[7/(3+1)] and its 20% Zn salt are shown in Figure 11. Both samples show about 10% hydrolytic scission of the imide group after 40 days. Plots of the ratio of anhydride peak at 1786 cm^{-1} to aromatic C-C stretch peak at 1582 cm^{-1} vs. time (days) for BTFMB27mP9[7/(3+1)] and its 20% Zn salt are shown in Figure 12. Figures 11 and 12 show that the 20% Zn salt of BTFMB27mP9[7/(3+1)] initially had a higher hydrolytic scission rate than the acid form. We think that Zn ion catalyzed the degradation, but was extracted out in 90°C water during the water stability test.

The dependence of the imide group hydrolysis on temperature was checked using FT-IR. The anhydride peak of BTFMB27mP9[7/(3+1)] after 20 days in 90°C water was about the same height as that of the copolymer kept under

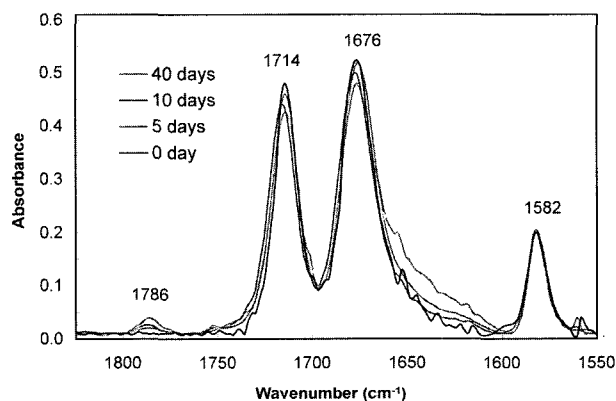


Figure 10. FT-IR spectra of 20% Zn salt of BTFMB27mP9[7/3+1] after 0, 5, 10 and 40 days in 90°C water, normalized to the aromatic C-C stretch peak at 1582 cm^{-1} .

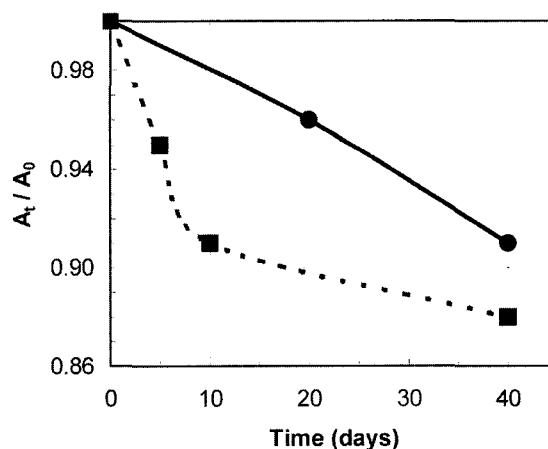


Figure 11. Plot of absorbance ratio, A_t/A_0 , vs. time for BTFMB27mP9[7/3+1] (solid line) and its 20% Zn salt (dotted line).

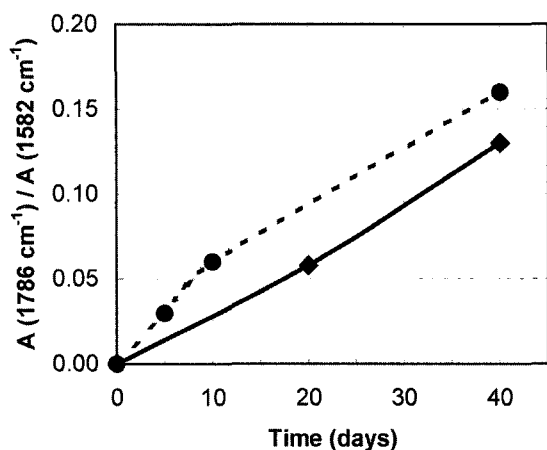


Figure 12. Plot of absorbance ratio, $A(1786\text{ cm}^{-1})/A(1582\text{ cm}^{-1})$, vs. time for BTFMB27mP9[7/3+1] (solid line) and its 20% Zn salt (dotted line).

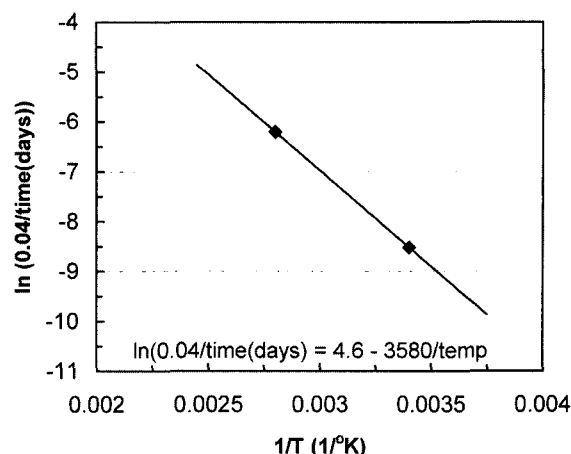


Figure 14. Arrhenius plot of $\ln(0.04/\text{time(days)})$ vs. $1/\text{temperature}$ for 4% decomposed BTFMB27mP9[7/(3+1)].

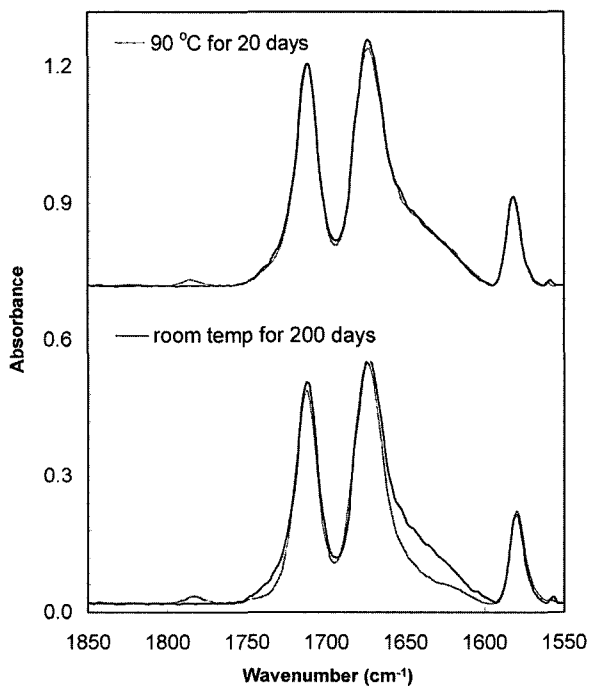


Figure 13. FT-IR spectra of BTFMB27mP9[7/3+1] (batch iv9) kept under different conditions.

ambient conditions for 200 days (Figure 13), which shows 4% hydrolytic scission of the imide group. Based on the Figure 13, we can obtain Arrhenius plot of $\ln(0.04/\text{time(days)})$ vs. $1/\text{temperature}$ for 4% decomposed BTFMB27mP9 [7/(3+1)] (Figure 14) and calculate an approximate activation energy (30 kJ/mol) from the slope of the plot.

Conclusions

The long-term stability of sulfonic acid containing poly-

imides was investigated using viscosity measurements and FT-IR analyses. The viscosities of homopolyimide and BTFMB27mP9[7/(3+1)] kept under ambient conditions were measured as a function of time. The viscosities decreased with time, with almost identical degradation rates. The degree of hydrolysis with time under ambient conditions and at elevated temperature in water was monitored by FT-IR analysis. A new absorption peak was observed at 1786 cm^{-1} , which corresponds to anhydride end groups by hydrolytic scission of imide rings. From the results of viscosity measurement and FT-IR analysis with time, we could calculate the initial degree of polymerization. The triisobutylamine and Zn salts of BTFMB27mP9[7/(3+1)] were prepared, hopefully to reduce the hydrolytic scission rate of the imide group. At $90\text{ }^\circ\text{C}$ in water, there was severe acid catalyzed hydrolytic degradation for all polymers.

Acknowledgements. This work is funded by DARPA (Grant F30602-97-2-0311).

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