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INTRODUCTION

As part of an effort to develop high performance structural resins with an attractive combination of properties for aerospace applications, a series of ethynyl-terminated polysulfones of different molecular weights were prepared and blended with a low molecular weight ethynyl-terminated coreactant. Upon heating above 200°C, these ethynyl containing materials react to form a chain extended and crosslinked network structure. This reaction renders the materials insoluble in common solvents but also reduces the toughness as compared to high molecular weight linear polysulfones. The purpose of this work is to thermally characterize ethynyl containing blends and to measure the toughness of the resulting cured materials.

A variety of polymers has been successfully crosslinked and/or chain extended by the thermal reaction of ethynyl end groups.[1] The use of 4-ethynylbenzoyl chloride (EBC) as an end-capping agent for hydroxy-terminated polysulfones,[2] hydroxy-terminated polyarylates,[3] and hydroxy-terminated poly(arylene ether ketones)[4] has been described elsewhere. Phenoxy resins have also been reacted with EBC to provide resins containing pendent ethynyl groups.[5] An excellent review of acetylene-terminated prepolymers has been published.[6]

EXPERIMENTAL

Monomers

4-Ethynylbenzoyl chloride (EBC) was prepared by reacting methyl 4-bromobenzoate with ethynyltrimethylsilane in the presence of dichlorobis(triphenylphosphine) palladium catalyst, followed by cleavage of the trimethylsilyl group using potassium carbonate, conversion of the methyl ester to acid with potassium hydroxide and finally to acid chloride using thionyl chloride. A detailed synthetic procedure for this compound has been reported.[3] 2,2-Bis(4-ethynylbenzoyloxy-4'-phenyl)propane (BEBOP) was prepared by reacting EBC with 2,2-bis(4-hydroxyphenyl)propane (BPA) in pyridine as shown in Eq. 1. The detailed synthetic procedure for this compound has also been reported.[3]

Oligomers

The hydroxy-terminated polysulfones (HTPS) at 2650, 5360 and 8890 g/mole number average molecular weights ($\overline{M}_n$) were obtained from Union Carbide Corporation (now Amoco Performance Products, Inc.)[7] and were used as received. The ethynyl-terminated polysulfones (ETPS) were prepared by reacting the HTPS with EBC in methylene chloride as shown in Eq. 2. The synthesis of ETPS-1 is given as an example of the synthetic procedure for all ETPS. HTPS-1 ($\overline{M}_n$=2650 g/mole, 300 g, 0.113 mol) was dissolved in methylene chloride (CH_2Cl_2) (900 ml) and triethylamine ($\mathcal{E}t_3N$) (27.4 g, 0.27 mol). EBC (40.98 g, 0.249 mol) in CH_2Cl_2 (250ml) was added slowly during 1 h, followed by stirring at room temperature (RT) for 16 h and 40°C for 2 h. Precipitation in methanol, followed by washing in methanol and boiling methanol and drying at 100°C provided a white polymer in essentially quantitative yield.

Blends

Polymer blends were prepared by pulvarizing the ETPS and BEBOP in a ball mill for several hours until they were homogenous in appearance. The 10% (weight %) blends contained 8 g BEBOP and 72 g of the appropriate ETPS while 20% blends contained 16 g BEBOP and 64 g of the appropriate ETPS providing an adequate amount of blend for the entire study.

Characterization

Inherent viscosities (η_{inh}) were obtained on 0.5% solutions in chloroform ($CHCl_3$) at 25°C. Differential scanning calorimetry (DSC) was performed at a heating rate of 20°C/min with the apparent glass transition temperature (T_g) taken at the inflection point of the ΔT versus temperature curve. Gel-permeation chromatography (GPC) was performed on a 10^6, 10^5, 10^4, 10^3 Å μ-Styragel column bank using $CHCl_3$ solvent, 2ml/min flow rate and a U.V. detector set at 254 nm.

Films

Small films were prepared by spreading $CHCl_3$ solutions of the blends (15% solids) onto plate glass and heating slowly to 250°C and holding at 250°C for 0.5 h. Films were then removed from the glass and subjected to flexibility and creasibility tests to qualitatively determine the toughness of the film.

Moldings

Blends (8 g) were compression molded in a 1.25 in. square stainless steel mold. Polymer filled molds were heated to 204°C, a pressure of 50 psi was applied (100 psi for blends containing ETPS-3) and held for 0.5 h followed by heating to 250°C, applying 100 psi pressure and holding an additional 0.5 h. Four compact tension specimens ~0.62 x 0.62 x 0.25 in. thick were cut from the 1.25 in. square molding and the critical stress intensity factor (K_{Ic}) was determined according to a known procedure.[8]

RESULTS AND DISCUSSION

Enough EBC and BEBOP was prepared following the literature procedures[3] for use throughout the study. Also, enough ETPS at each molecular weight was prepared beforehand so all blends are made from the same batch of BEBOP and ETPS, thereby eliminating differences in materials which can arise from using different batches of precursor.

The HTPS and ETPS oligomers were characterized as shown in Table 1. The HTPS were obtained from Union Carbide Corporation with the experimentally determined $\overline{M}_n$s provided. The $\overline{M}_n$s of the ETPS were calculated using these $\overline{M}_n$s and adding the molecular weight of the two ethynyl containing end-groups. As expected, the η_{inh}s increased with increasing molecular weight for both the HTPS and the ETPS. The HTPS were also subjected to GPC analysis and results are presented in Table 1. A decrease in GPC peak retention time from 19.46 to 18.13 min is observed for increasing molecular weight from 2650 to 8890 g/mole, respectively. The peaks were relatively broad with a typical Gaussian molecular weight distribution characteristic of step-growth polymers. The last two columns in the table show DSC T_gs. The initial T_gs increase with increasing molecular weight for both series of oligomers. However, after curing 0.5 h at 300°C, the T_gs of the ETPS display the opposite trend, decreasing from 200°C to 197°C for increasing precursor molecular weight. These results were expected since lower molecular weight precursor leads to higher crosslink density in the cured material.

In an effort to better understand and correlate the data, the weight percentage of ethynyl groups present in each polymer blend was calculated and is shown in Table 2. Ethynyl group content ranged from 3.4 weight % for ETPS-1/20% BEBOP to 1.5 weight % for ETPS-3/10% BEBOP. The blend with the highest molecular weight ETPS and 20% BEBOP had almost the same weight % ethynyl groups as the blend with the lowest molecular weight ETPS with 10% BEBOP (2.5 and 2.6%, respectively).

The polymer blends were characterized by DSC and results are presented in Table 2. This table lists initial T_gs, endotherm minimums, exotherm maximums and cured T_g. The DSC curves for ETPS-1/10% BEBOP are shown in Figure 1 as a typical example of the blends. This blend has an initial T_g at 155°C, endothermic peaks at 160 and 180°C and the exothermic peak at 245°C. The bottom curve is a rerun of the same sample after holding 0.5 h at 300°C and displays a cured T_g of

208°C with no additional exotherm. The only other blend to display two endothermic peaks also contained ETPS-1. All blends had an endothermic peak in the 180-183°C region as well as an exothermic peak in the 240-245°C region. Although exothermic peak positions are essentially the same, peak areas are different and correspond to the amount of ethynyl groups present (i.e. the ETPS-1/20% BEBOP exothermic peak is the largest and the ETPS-3/10% BEBOP exothermic peak is the smallest). The cured T_gs also reflect the amount of ethynyl groups present, with the ETPS-1/20% BEBOP having the highest T_g and the ETPS-3/10% BEBOP having the lowest T_g. However, when the weight % of ethynyl groups present is almost constant, blends containing higher molecular weight ETPS had lower T_gs (ETPS-3/20% BEBOP, T_g=198°C compared to ETPS-1/10% BEBOP, T_g=208°C).

Small area films were prepared in an effort to qualify film toughness. The first column in Table 3 gives results of simple crease tests on films cured 0.5 h at 250°C. The film from ETPS-1/20% BEBOP was extremely brittle and broke apart when removed from the glass plate. The films from both blends of ETPS-3 could be folded over and creased without breaking. The remaining films were flexible but would break upon creasing.

Moldings of the blends were prepared under the conditions noted in Table 3 and the K_{Ic} was determined. The first two blends containing ETPS-1 had low toughness and K_{Ic} values reported are the average of only two specimen since other specimen broke upon machining. The remaining K_{Ic} values are the average of four samples with about 15%

standard deviation. These blends display a K_{Ic} which is inversely proportional to weight % ethynyl groups present, ranging from 800 psi • $in^{1/2}$ for ETPS-2/20% BEBOP to 1520 psi • $in^{1/2}$ for ETPS-3/10% BEBOP. The G_{Ic} is calculated by squaring the K_{Ic} and dividing by the modulus. The modulus was not measured for each blend so a value of 355 ksi was chosen from a previous report[9] for an ETPS with $\overline{M}_n \approx$ 12,000 g/mole. The G_{Ic}s range from 1.3 to 6.5 in lb/in,^{2} tougher than conventional epoxies ($G_{Ic} \sim 0.5$ in lb/in^2) but less tough than high molecular weight polysulfone ($G_{Ic} \sim 18$ in lb/in^2).

CONCLUSIONS

A series of ethynyl-terminated polysulfones with different number average molecular weights were prepared and blended with various amounts of a low molecular weight ethynyl-terminated coreactant. The blends were thermally characterized, moldings were prepared and the critical stress intensity factor was determined. The resulting values were found to be inversely proportional to ethynyl group content ranging from 680 to 1520 psi • $in^{1/2}$, which is tougher than epoxies but less tough than high molecular weight polysulfone.

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TABLE 1. Characterization of Polymers

Polymer	$\overline{M}_n$,g/mole	η_{inh}, dL/g[a]	GPC Peak Retention Time, min[b]	DSC, °C[c]	
				Initial T_g	Cured T_g[d]
HTPS-1	2650	0.10	19.46	152	152
HTPS-2	5360	0.16	18.70	174	174
HTPS-3	8890	0.25	18.13	182	182
ETPS-1	2906	0.10	-----	157	200
ETPS-2	5616	0.17	-----	175	198
ETPS-3	9146	0.26	-----	181	197

[a] Inherent viscosity, 0.5% solution in chloroform at 25°C.

[b] GPC using $CHCl_3$ solvent, 2ml/min flow rate, μStyragel columns (10^6,10^5,10^4,10^3Å), U. V. detector (254 nm).

[c] DSC at a heating rate of 20°C/min.

[d] Cured 0.5h at 300°C.

TABLE 2. Characterization of Polymer Blends

Polymer Blend	Ethynyl Content Weight %	DSC, °C[a]			
		Initial T_g	Endotherm Minimums	Exotherm Maximums	Cured Tg[b]
ETPS-1/10% BEBOP	2.6	155	160,180	245	208
ETPS-1/20% BEBOP	3.4	157	163,180	242	213
ETPS-2/10% BEBOP	1.8	172	183	242	198
ETPS-2/20% BEBOP	2.8	172	182	242	200
ETPS-3/10% BEBOP	1.5	176	182	245	198
ETPS-3/20% BEBOP	2.5	177	183	240	198

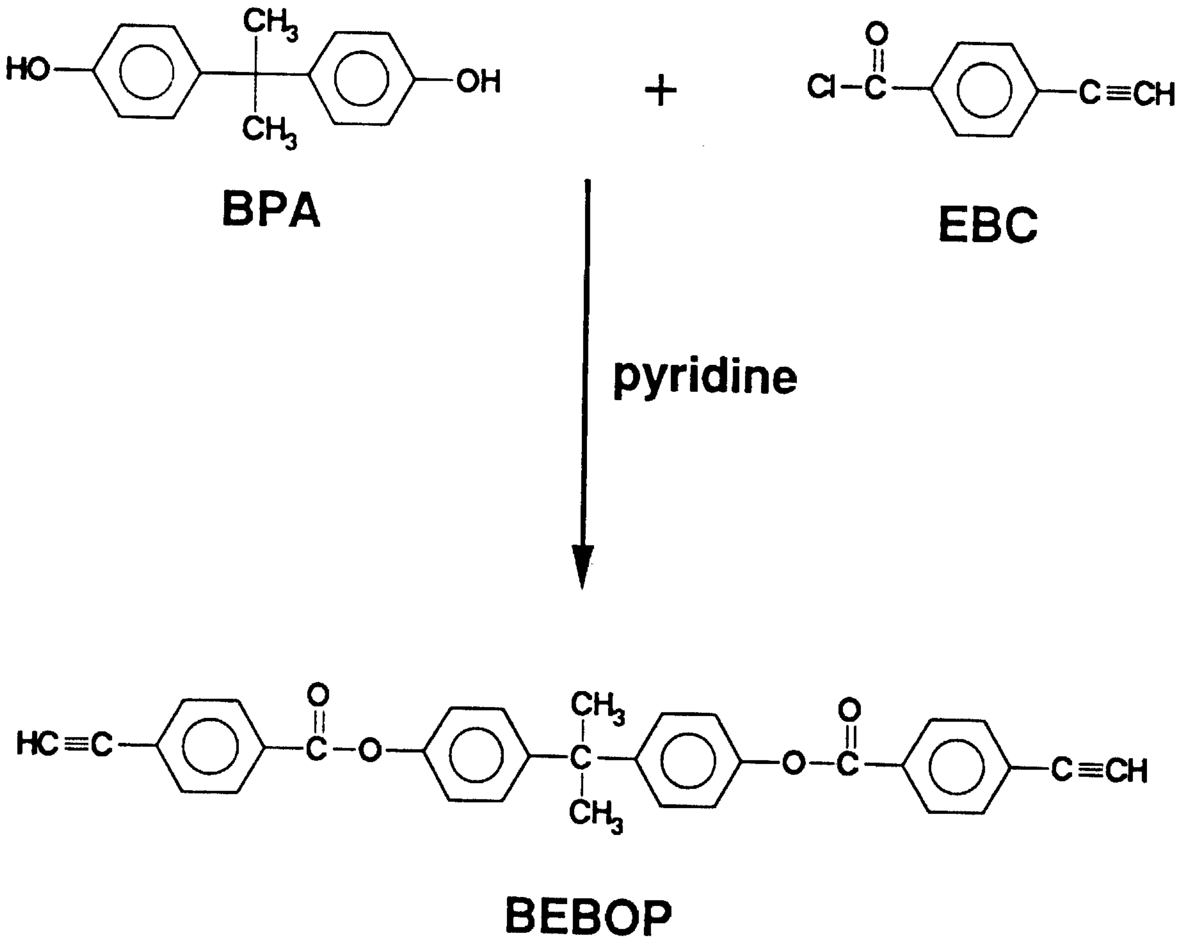
[a] DSC at a heating rate of 20°C/min.

[b] Same sample rerun after holding 0.5 h at 300°C.

TABLE 3. Toughness of Polymer Blends

Polymer Blend	Films[a]	Moldings	
		K_{Ic}, psi • in$^{1/2}$	G_{Ic}, in lbs/in^2
ETPS-1/10% BEBOP[b]	flexible	680[d]	1.3
ETPS-1/20% BEBOP[b]	brittle	770[d]	1.7
ETPS-2/10% BEBOP[b]	flexible	1230[e]	4.3
ETPS-2/20% BEBOP[b]	flexible	800[e]	1.8
ETPS-3/10% BEBOP[c]	creasible	1520[e]	6.5
ETPS-3/20% BEBOP[c]	creasible	1160[e]	3.8

[a] Films cured 0.5 h at 250°C.
[b] Molded 0.5 h at 204°C and 50 psi then 0.5 h at 250°C and 100 psi.
[c] Molded 0.5 h at 204°C and 100 psi then 0.5 h at 250°C and 100 psi.
[d] Average of two samples
[e] Average of four samples



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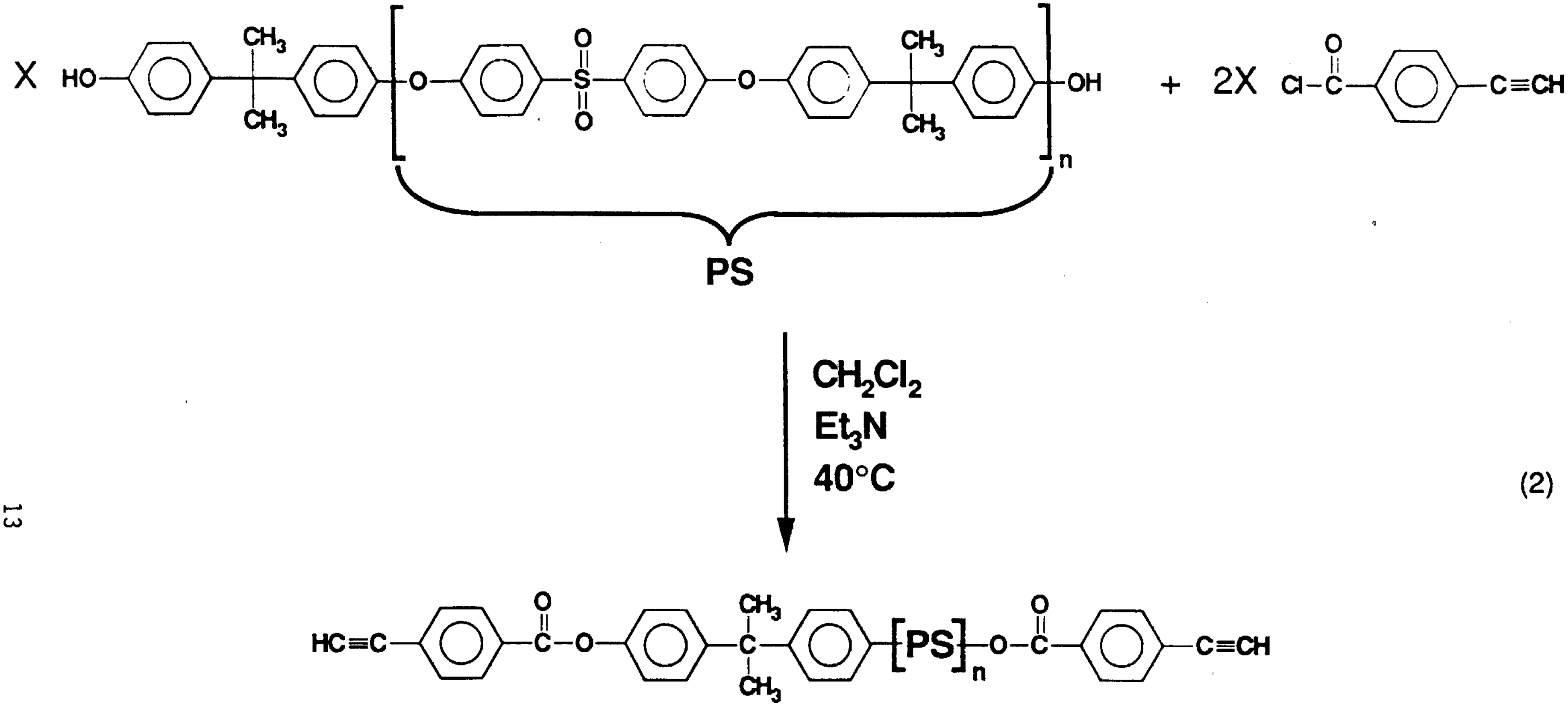

(2)

For $\overline{M}_n$ (g/mole)	then n
2650	~5.5
5360	~11.5
8890	~19.5

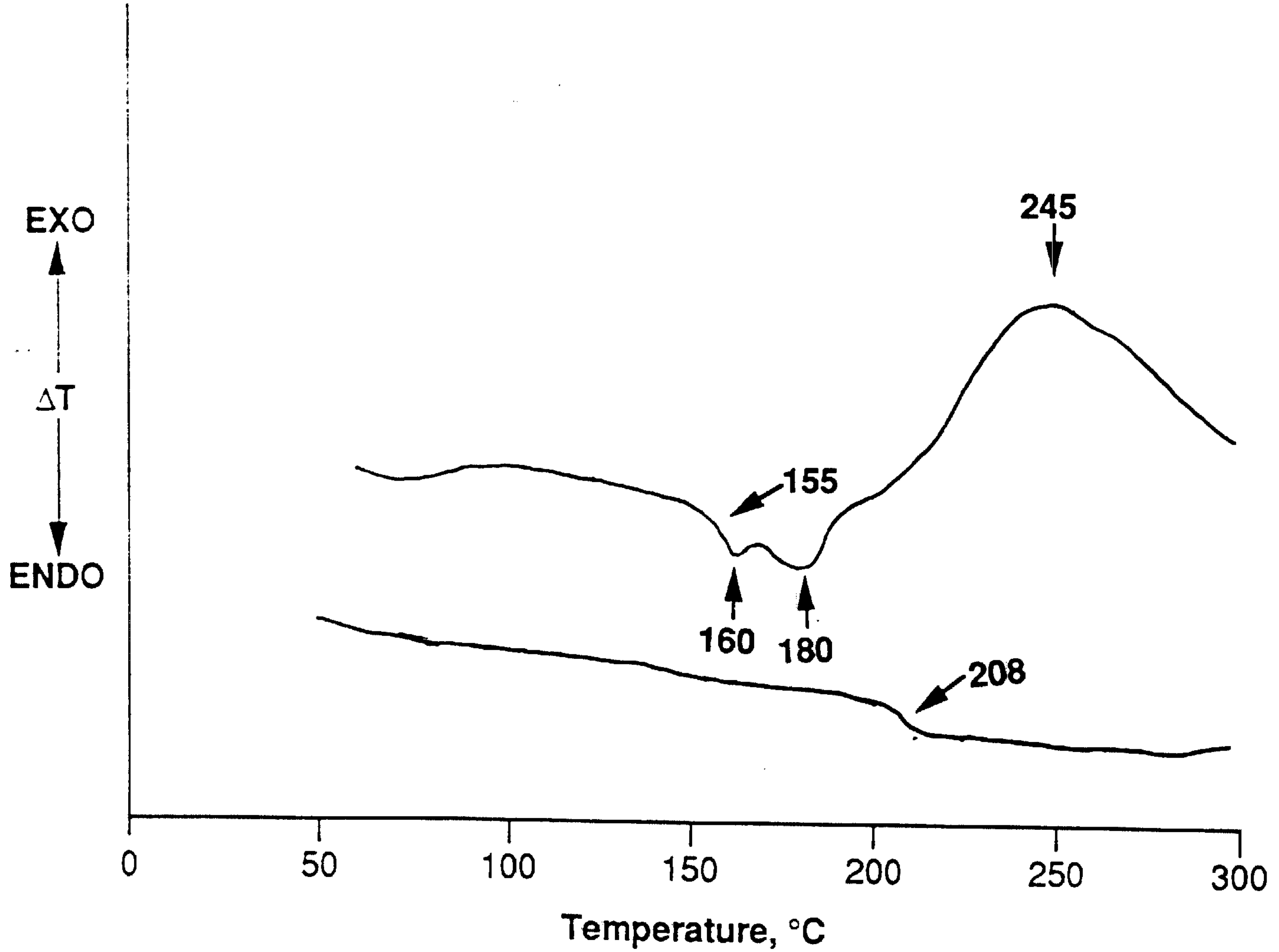

Figure 1. DSC thermograms of ETPS-1/10% BEBOP.

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16. Abstract

As part of an effort to develop high performance structural resins with an attractive combination of properties for aerospace applications, a series of ethynyl-terminated polysulfones of different molecular weights were prepared and blended with a low molecular weight ethynyl-terminated coreactant. Upon heating above 200°C, these ethynyl containing materials react to form a chain extended and crosslinked network structure. This reaction renders the materials insoluble in common solvents but also reduces the toughness as compared to high molecular weight linear polysulfones. This work discusses the thermal characterization of these blends and the toughness of the resulting cured materials.

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