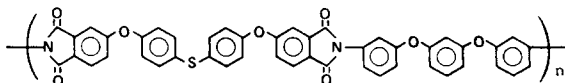


NOTE

The Effect of Molecular Weight on the Melt Viscosity and Fracture Energy of BDSDA/APB

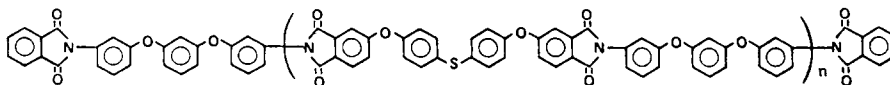
INTRODUCTION

In a previous report,¹ the synthesis and characterization of a novel linear aromatic polyphenylene ether sulfideimide (BDSDA/APB) was described. The chemical structure of this material is shown below. This polymer, having been molded, used as an adhesive, and cast into thin films, seemed



Scheme 1

well suited for processing via conventional thermoplastic methods. In an effort to improve the use properties and processability of BDSDA/APB, its molecular weight was varied by endcapping with phthalic anhydride. This approach was taken because of the work previously reported by Fox and Flory.² They found that decreasing the molecular weight of polystyrene caused its melt viscosity to decrease. The effect of changing molecular weight was determined by measuring the melt viscosity and fracture energy (G_{Ic}) values for the different endcapped polymers whose chemical structure is shown below.



Scheme 2

EXPERIMENTAL

Polymer Synthesis. To form the uncapped polymer, 1.000 molar ratio of 4,4'-bis(3,4-dicarboxyphenoxy)diphenylsulfide dianhydride (BDSDA) and 1.000 molar ratio of 1,3-bis(aminophenoxy)benzene (APB) were dissolved in bis(2-methoxyethyl)ether at a 15% solids level in a flask equipped with magnetic stirring. This solution was allowed to stir for 1 h in order for molecular weight to build.

In the case of the endcapped systems the appropriate amount of APB was dissolved in the bis(2-methoxyethyl)ether and the endcapping agent, phthalic anhydride (PA), was added, and the system was stirred for 15 min. Next the BDSDA was added and stirring continued for one hour to again allow molecular weight to build. Table I shows the ratios of reactants that were used for the different endcapped systems. Note that since the BDSDA is difunctional, the decrease of 1% in this constituent must be offset with a concomitant increase of 2% in the PA which is monofunctional. This is done to maintain proper stoichiometry of amine to anhydride.

Molding Powder Preparation. The polymer solutions were poured into a mechanical blender containing distilled water. The contact with water caused the poly(amic acid) to precipitate, and the rotating blender blades chopped this material into a fluffy consistency. The solid polymer was isolated by suction filtration and allowed to air dry overnight.

Each dried polymer was spread in a baking dish, placed in a forced-air oven, and heated to 100°C. The polymer was held at this temperature for 1 h to drive off residual water and solvent. The temperature was increased to 200°C and held for 1 h to effect conversion of amic acid to the imide.

Molding Preparation. The polyimide powders were molded into discs according to the following procedure. The imidized powder was placed in a matched-metal molding die which was preheated to 160°C. A pressure of 1.38–2.07 MPa (200–300 psi) was applied to effect consolidation. This temperature and pressure were held for 0.5 h. The mold was allowed to cool to approximately 100°C, and the molding was removed.

TABLE I
Molar Ratios of Reactants for Endcapped Systems

PA, Percent	APB, mole ratio	BSDA, mole ratio	PA, mole ratio
1%	1.000	0.995	0.010
2%	1.000	0.990	0.020
4%	1.000	0.980	0.040

Rheology. Melt flow properties were determined at 250°C and 280°C using a capillary rheometer (Instron Model 3211).³ The capillary used had a length-to-diameter ratio of 33; therefore, no end corrections were required.

Mechanical Testing. The fracture energy values (G_{Ic}), the opening mode strain energy release rates, were determined for one sample each of 0%, 1%, 2%, and 4% endcapped BSDA/APB. The samples were machined from discs 5.715 cm diameter and nominally 0.127 cm thick, precracked, and tested according to ASTM Standard E399-78A. They were run at a crosshead speed of 0.127 cm/min.

Molecular Weight. The number-average molecular weight (\bar{M}_n) was determined at room temperature for the poly(amic acid) dissolved in tetrahydrofuran. A Knauer Membrane Osmometer was used for the \bar{M}_n measurements. (Molecular weight determined by ARRO Laboratory, Joliet, Illinois.)

RESULTS AND DISCUSSION

The poly(amic acid)s that were prepared as previously described were characterized by inherent viscosity (η_{inh}) measurements at 35°C. There was a trend towards lower viscosity as the end group concentration increased, i.e., η_{inh} of 0.66, 0.35, 0.31, and 0.35 dL/g for the polymers containing 0%, 1%, 2%, and 4% phthalic endcaps, respectively. All of the polymers had similar appearances after precipitation and subsequent imidization. All of the powders had adequate flow at 160°C to effect consolidation. During the molding operation it was evident that flow was increasing with increasing endcaps. The number-average molecular weights (\bar{M}_n) for the series of poly(amic acid)s were found to be lower with increasing endcapping, i.e., \bar{M}_n of 13,900, 9970, 8780, and 8660 for the polymers containing 0%, 1%, 2%, and 4% phthalic endcaps, respectively. Up to 2% endcapping this trend paralleled the inherent viscosity data.

A major objective of this research was to determine the effect of \bar{M}_n on melt-flow properties of this polymer (BSDA/APB). Based on the work of Fox and Flory,² it was expected that as the \bar{M}_n decreased the melt flow would increase. However, the degree of change must be determined for each individual polymer system. In the endcapped polyimide study there was a direct relationship between \bar{M}_n and apparent viscosity as shown in Figure 1. At 250°C there was no deviation from linearity, but at the higher extrusion temperature of 280°C the viscosity dropped precipitously for the systems with an \bar{M}_n below 10,000. The apparent viscosity of the 4% endcapped material was too low at 280°C for the capillary rheometer to measure. Particularly noteworthy was the drop of 2 orders in magnitude for the apparent viscosity at 250°C when the \bar{M}_n changed from approximately 14,000 to 8700. This information should be valuable in optimizing processibility.

When moldings were prepared from the different molecular weight polymers, it was obvious that the higher \bar{M}_n systems resisted cracking more than the lower \bar{M}_n systems. The G_{Ic} data proved that a considerable loss in fracture resistance does occur as the molecular weight decreases. This relationship is shown in Figure 2. Of particular interest was that, over the range tested, the G_{Ic} value was linearly related to the number-average molecular weight. The steep slope of this relationship was quite surprising. A change in \bar{M}_n from 14,000 to 10,000 resulted in nearly a 3000 J/m² loss in G_{Ic} .

In summary, the change in \bar{M}_n from 14,000 to 8700 resulted in a dramatic decrease in the apparent viscosity at both 250°C and 280°C when the rheological properties of the polymer system were studied. The G_{Ic} values for these same molecular weight materials decreased in a like manner as the \bar{M}_n decreased. From this \bar{M}_n vs. viscosity and G_{Ic} data, it is obvious that tradeoffs can be made

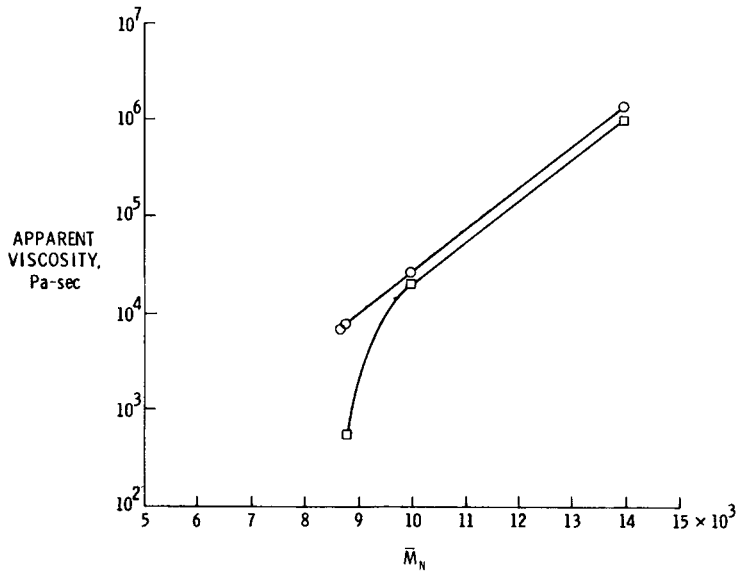


Fig. 1. Apparent viscosity as a function of molecular weight (\bar{M}_n) of BDSDA/APB at (○) 250°C and (□) 280°C. Strain rate = 1.346 s⁻¹.

between process optimization and final mechanical properties when polymer systems are developed.

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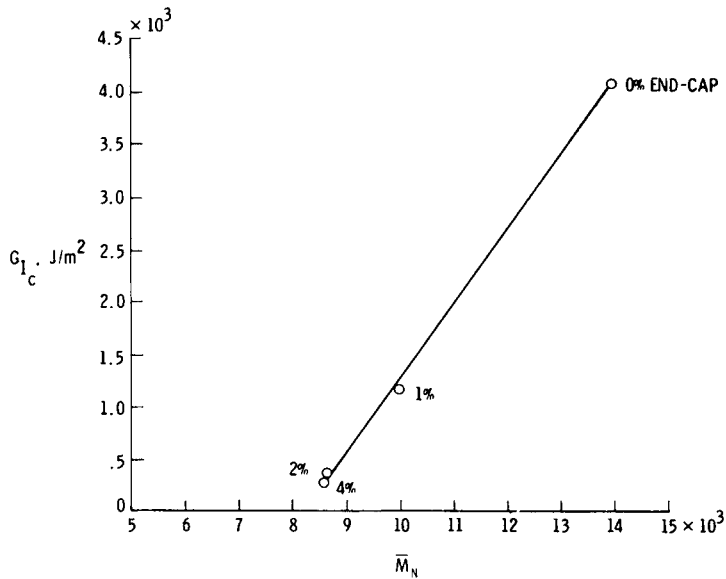


Fig. 2. The fracture energy (G_{Ic}) as a function of molecular weight (\bar{M}_n) of BDSDA/APB.

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