

UNIVERSITY OF SOUTH AUSTRALIA

**CRYSTALLINITY IN LINEAR POLYAMIDES: A STUDY  
USING MELT BLENDING WITH SMALL-MOLECULE  
DILUENTS**

by

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## GLOSSARY OF TERMS

|              |   |
|--------------|---|
| Aramid       | Polyamide with aromatic groups in the main chain  |
| ATR          | Attenuated Total Reflection   |
| Dalton       | One twelfth of the mass of a carbon-12 atom in its ground state                               |
| DRIFT        | Diffuse Reflection Infrared Fourier Transform   |
| DSC          | Differential Scanning Calorimeter   |
| DTA          | Differential Thermal Analysis   |
| FTIR         | Fourier Transform Infrared  |
| G            | Free Energy (Gibbs)   |
| H            | Enthalpy  |
| $\Delta H_f$ | Heat of Fusion  |
| iPP          | Isotactic poly(propylene)   |
| l            | Length  |
| LCST         | Lower Critical Solubility Temperature   |
| $\mu_i$      | Chemical potential equivalent to the partial molar Gibbs Free energy of a mixture constituent |
| MAS          | Magic Angle Spinning  |
| Mn           | Number average molecular weight   |
| MTDSC        | Modulated Temperature Differential Scanning Calorimetry                                       |
| $M_w$        | Weight average molecular weight   |
| NIR          | Near Infra Red range covering wavenumbers between 11,000 and 4,000 $\text{cm}^{-1}$ .         |
| NMR          | Nuclear Magnetic Resonance  |
| Nylon        | Aliphatic polyamide   |
| PA-n         | Polyamide-n where n is the number of carbon atoms per repeat unit                             |
| PA-m,n       | Polyamide-m,n where m and n are the number of carbon atoms per diamine and diacid repeat unit |
| PA46         | Polyamide-4,6   |
| PA46Car      | Polyamide-4,6/carbazole blend   |
| PA46PTh      | Polyamide-4,6/phenothiazine blend   |
| PA6          | Polyamide-6   |

|               |  |
|---------------|--|
| PA6Car        | Polyamide-6/carbazole blend  |
| PA6PTh        | Polyamide-6/phenothiazine blend  |
| PA69          | Polyamide-6,9  |
| PA69Car       | Polyamide-6,9/carbazole blend  |
| PA69PTh       | Polyamide-6,9/phenothiazine blend  |
| PA612         | Polyamide-6,12   |
| PA612Car      | Polyamide-6,12/carbazole blend   |
| PA612PTh      | Polyamide-6,12/phenothiazine blend   |
| PAS           | PhotoAcoustic Spectroscopy   |
| PEG           | Poly(ethyleneglycol)   |
| PEO           | Poly(ethyleneoxide)  |
| PVDF          | Poly(vinylidene fluoride)  |
| R             | Gas Constant   |
| Reptate       |  |
| S, $\Delta S$ | Entropy, Entropy change  |
| SAXS          | Small Angle X-ray Scattering   |
| SDT           | Simultaneous Differential Thermal Analysis –<br>Thermogravimetric Analysis |
| t             | Time   |
| T             | Absolute Temperature ( $^{\circ}\text{K}$ )                                |
| $T_B$         | Brill temperature  |
| $T_c$         | Peak crystallisation temperature   |
| $T_g$         | Glass Transition Temperature   |
| TLS peak      | Temperature Limited Solubility peak (see Section 1.5.2.2)                  |
| $T_m$         | Peak melting temperature   |
| TGA           | Thermogravimetric Analysis   |
| TIPS          | Thermally Induced Phase Separation   |
| TMDSC         | Temperature Modulated Differential Scanning Calorimetry                    |
| UCST          | Upper Critical Solubility Temperature                                      |
| V             | Volume   |
| WAXD          | Wide Angle X-ray Diffraction   |

## ABSTRACT

Linear polyamides, commonly known as Nylons, are widely used for their high melting temperatures, heat stability, toughness and abrasion resistance, allowing diverse commercial applications such as carpets, nylon stockings and automotive parts. The work here has possible ramifications for membrane production and drug delivery systems and makes a scientific contribution to the area of binary polymer/diluent systems where the polymer is semicrystalline and the diluent crystallises at a quite different temperature to the polymer. Melt blended crystalline/crystalline systems have, so far, not received the attention that amorphous/amorphous or crystalline/amorphous systems have, perhaps due to the complexity of the morphology that often results within such systems.

The polyamide-4,6, polyamide-6, polyamide-6,9, and polyamide-6,12 studied here are representative of the range of available linear polyamides. The organic diluents were initially chosen as potential hydrogen bond disruptors. Investigative techniques concentrated on Differential Scanning Calorimetry and Fourier transform infrared spectroscopy. Thermogravimetric Analysis was also used for the determination of diluent levels in samples.

It was found that melt blends where the crystallisation temperature of the undiluted polyamide is less than that of the neat diluent lead to characteristic solidification during slow cooling at 2 °C/min. Here, there is a linear drop off in enthalpy of crystallisation for the diluent component of the blend. This reaches zero near the “eutectic” composition. There are no endothermic peaks at the “eutectic” temperature for blends where polyamide is in excess of the eutectic composition.

There is depression of polymer and diluent crystallisation by each other in direct proportion to the concentration of the other material when the crystallisation temperature relationships are reversed. A wider scatter in the enthalpy of crystallisation of the diluent component ensues. Prior crystallisation close to the polyamide crystallisation temperature is more probable, especially when the cooling rate is greater.

The range of polyamides studied shows the effects of polyamide repeat structure on eutectic compositions and on the maximum crystallisation and melting depressions for the three polyamides having relatively close melting temperatures.

Choosing the diluents as probable model polyamide-polyamide hydrogen bond disruptors has potentially been important for a variety of applications. Hydrogen bond donor groups of the two diluents have been found not to interact with the carbonyl acceptors in the solidified polyamides. Fourier transform infrared spectroscopy (FTIR) carried out with photoacoustic spectroscopy in the Mid Range IR on all blend samples have found no evidence of N-H peak shifts that differ from simple summation of the spectra. This point is supported by Near Infra-Red experiments on all blends using the DRIFT technique in sensitive hydrogen bonding overtone regions.

Some information in the Mid Range IR band 1700 to 400  $\text{cm}^{-1}$  is ambiguous because of the non-linear response of photoacoustic measurements. In addition, very bright pink colours were observed in some samples, implying pi-conjugation or charge transfer processes.

The thesis includes discussion in an appendix on the general applicability of Temperature Modulated Differential Scanning Calorimetry and the use of Lissajous figures to evaluate experimental conditions such as purge gas type and flow rates.

## **DECLARATION**

To the author's knowledge and belief, the material in this thesis, except where due reference is made or where common knowledge is assumed, is original. No part of this work has been submitted for any other degree or award in any university.

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