EFFECT OF STRUCTURE ON THERMAL CHARACTERISTICS OF POLYMERS DERIVED FROM NADIMIDES AND BISNADIMIDES

by

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CERTIFICATE

This is to certify that the thesis entitled '**EFFECT OF STRUCTURE ON THERMAL CHARACTERISTICS OF POLYMERS DERIVED FROM NADIMIDES AND BISNADIMIDES**' being submitted by **Ms. Rajni Madan** to the Indian Institute of Technology, Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. Ms. Rajni Madan has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis which to our knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

This thesis deals with the evaluation of thermal behaviour of polymers derived from nadimides and bisnadimides using ring opening metathesis polymerisation (ROMP), carbocationic polymerisation and thermal polymerisation techniques. ROMP gave polymers with unsaturation in the backbone whereas carbocationic and thermal polymerisation gave saturated polymers. These nadimides were synthesised by reacting nadic anhydride with aromatic amines.

The *endo* form of nadic anhydride has been reported in the literature to be inert to ROMP. Therefore, thermal isomerisation of nadic anhydride was carried out at 190°C in order to convert the commercially available *endo* nadic anhydride into thermodynamically more stable *exo* form. The conditions of thermal isomerisation were optimised and the *endo* and *exo* isomers were characterised by FTIR and ^{1}H NMR.

N-phenyl nadimide and N-*o/m/p*-tolyl nadimides were synthesised by reacting *endo/exo* nadic anhydride with the corresponding amine at 120°C in glacial acetic acid. The melting points were dependent upon the *exo* content in the sample. The monomers were characterised by ^{1}H NMR and FTIR. ROMP of nadimides was carried out using WCl_6/tetramethyltin catalyst system in chlorobenzene at 70°C. A glove box was used for transfer of catalyst due to its sensitivity to moisture and air. Only *exo* nadimides could be polymerised whereas the *endo* isomer was inert to ROMP. The conditions of polymerisation (duration, M/W/Sn) were optimised. The polymers were characterised by FTIR, ^{1}H NMR, GPC and thermal techniques. The [η] of poly(N-aryl nadimides) in $CHCl_3$ at 30°C varied from 38.5 to 44.5 mL/g. The $\bar{M}n$ and $\bar{M}w$ determined from GPC varied from 8.5 x10^4 to 16.5x10^4 g/mol. The T_g of poly (N-*o/m/p*-tolyl nadimides) were

found to be 233, 196 and 221°C respectively. The polymers showed one step decomposition and T_i, T_f and T_{max} were 443 ± 3, 499 ± 1 and 471 ± 3°C respectively.

Carbocationic polymerisation of N-*o/m/p*-tolyl nadimides was done using Pd(II) catalyst which was synthesised in the laboratory. The effect of different parameters such as duration, monomer/ catalyst molar ratio, temperature, position of substituent, gegen ion and solvent on % yield and molecular weight was studied. Under similar conditions of polymerisation, poly(N-*m*-tolyl nadimide) showed higher molecular weight (33487g/mol) compared to poly (N-*o*-tolyl-nadimide) (10134g/mol) and poly(N-*p*-tolyl nadimide) (24241 g/mol). The polymers showed higher thermal stability than the polymers derived from ROMP. The values of T_i, T_f and T_{max} were higher by 25-30°C compared to polymers derived from ROMP.

Bisnadimides containing different structures were synthesised by reacting nadic anhydride (*endo/exo*) with the : 1,4-1,3-*bis* (4'-aminophenoxy)benzene(Q/R), 2,2'-*bis*[4-(4'-aminophenoxyphenyl]propane (B) and *bis*[4-(4'-aminophenoxy) phenyl] sulphone (S). The diamines were synthesised by reduction of the corresponding dinitro compounds with Pd/C and hydrazine hydrate. The bisnadimides were characterised by FTIR, ^{1}H NMR and thermal techniques.

The bisnadimides were subjected to both ROMP and thermal polymerisation. ROMP was carried out using WCl_6/tetramethyltin catalyst system under optimised polymerisation conditions. Thermal polymerisation was done at 300°C for 30min. The polymers obtained were insoluble in most of the organic solvents and were characterised by FTIR, DSC and TG. There was no significant difference in thermal stability of the polymers derived from thermal curing of *endo* and *exo* bisnadimides.

A comparison of the thermal stability of polymers derived from ROMP and thermal polymerisation indicated higher % char yield for polymers derived from

ROMP (54-72%) compared to those derived by thermal polymerisation (39-50%). The thermally cured polymers showed one step decomposition above 450°C whereas polymers obtained by ROMP showed a two step decomposition.

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CHAPTER VI THERMAL CHARACTERISATION OF POLYMERS

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