

Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

THERMAL BEHAVIOUR OF POLYMERS BASED ON NADIMIDES

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Abstract

Carbocationic polymerization of *N-ortho/meta/para* tolyl-exo-norbornene dicarboximide (nadimide) was carried out using Pd(II) catalyst. Under similar conditions of polymerization, poly(*N-m*-tolyl nadimide) showed higher molecular mass compared to poly(*N-p*-tolyl nadimide) and poly(*N-o*-tolyl nadimide). Thermal stability of these polymers was evaluated by dynamic thermogravimetry in nitrogen atmosphere. The polymers were stable up to 460°C and lost mass above this temperature in a single step. The characteristic decomposition temperature and char yield of these polymers were higher than the polymers prepared by using ring opening metathesis polymerization. The difference has been attributed to the presence of rigid bicyclic ring structure in these polymers.

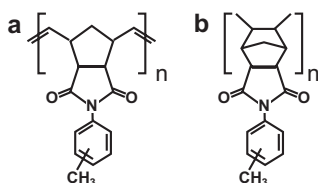
Keywords: carbocationic polymerization, char yield, *N*-aryl nadimides, ring opening metathesis polymerization (ROMP), thermal stability

Introduction

Endo-5-norbornene-2, 3-dicarboximides (nadimides) constitute an important class of resins which were introduced in the beginning of 1970's to meet the increasing demands for heat resistant matrix resins for aerospace and military applications. These low molecular mass oligomers cure at high temperature to yield a cross linked polymer network with high T_g and good performance in hot-wet environment.

Nadimides are versatile monomers capable of undergoing ring opening metathesis polymerization (ROMP) as well as carbocationic polymerization. The structure of the polymer formed by these techniques is markedly different. Therefore nadimides offer a unique opportunity to study the effect of structure on properties of polymers. The structures of polymers obtained by polymerization of *N-o/m/p*-tolyl nadimides (*N-1/N-2/N-3*, respectively) using different techniques can be seen on the next page:

Highly strained ring compounds such as 5-norbornene-2,3-dicarboxy anhydride have been successfully polymerized using metathesis reaction [1–5]. Ring opening metathesis polymerization of *N*-methyl exo-norbornene dicarboximide in dichloroethane solution has been reported to yield polymers with high T_g (220°C) and a number average molecular mass of 25,000. The catalysts used were WCl_6 -acetal (mole ratio 1:2 in toluene) and diethyl aluminium chloride (in heptane). Ruthenium tri-



Scheme 1 Representative structures of polymers prepared from N-tolyl nadimides by (a) ROMP (polymers designated as PN-1/PN-2/PN-3 based on N-1, N-2 and N-3 monomers respectively), (b) carbocationic polymerization (polymers designated as AN-1/AN-2/AN-3)

chloride trihydrate (in butanol), osmium trichloride (in chlorobenzene, ethanol), or iridium chloride (in chlorobenzene, ethanol) were other catalysts used for this polymerization.

The *exo* isomer of N-phenyl norbornene dicarboximide could also be polymerized into a high molecular mass straight chain polymer using different catalyst: co-catalyst systems [6]. The structure of the polymer was dependent on the type of initiator used. Ruthenium and osmium catalysts produced predominantly *trans* structure of the double bond while WCl_6 /aluminium alkyl catalyst yielded a mixture of *cis* and *trans* isomers. The T_g of the *trans* isomer was $\sim 15^\circ C$ higher ($240^\circ C$) than the *cis* isomer ($225^\circ C$). A 53:47 mixture of *exo:endo* isomers of N-phenyl nadimide could also be polymerized to approx. 50% conversion [7]. N-phenyl *exo* norbornene dicarboximides having electron withdrawing substituents like fluoro, chloro or bromo at *ortho*, *meta* and *para* positions or electron donating methyl groups have also been polymerized using WCl_6/Et_2AlCl or $WCl_6/SnMe_4$ as catalysts and toluene or 1,2-dichloroethane as a solvent [8, 9]. The substituent group and its position on the phenyl ring did not affect the stereochemistry of the *cis* content in these polymers which ranged from 33 to 43% [8].

Considerable work has also been done in our laboratories on bisnadimide resins which were thermally polymerized to yield highly cross linked networks [10–14].

Carbocationic polymerization of substituted polynorbornene has been reported in literature [15, 16]. Palladium catalyst have been employed earlier for addition polymerization of norbornene derivatives containing ester groups [15]. The advantage offered by these catalysts is the increased tolerance to polar functional groups. Initial experiments with $Pd(CH_3CN)_4BF_4$ in dry acetonitrile were a failure but addition of a small amount of water resulted in a slow propagation (yield-20% after three weeks of reaction, M_n -11000). $PdCl_2/H_2O$ gave only 20% yield in two days. However palladium complexes with multidentate coordinating ligands have been found to be more reactive and have been reported to give 99% yield in 2 min.

Carbocationic polymerization of N-aryl nadimides has not been reported in the literature. It was therefore, considered of interest to study vinylic polymerization of *exo o-/m-/p*-tolyl nadimides. In view of the profound constraints in the monomer, the polymer is expected to be quite rigid and thermally stable. In this paper we report thermal behaviour of these polymers. Comparison with thermal stability of polymers prepared by ROMP [9] is also made.

Experimental

Materials

Toluene (Qualigens Fine Chemicals) was dried by passing sodium wire. Acetic acid (BDH), chlorobenzene (Qualigens Fine Chemicals) were distilled before use. Aniline (S.D. Fine Chemicals), *o*-toluidine (Merck) and *m*-toluidine (Koch Chemical Lab.) were distilled under nitrogen before use, *p*-toluidine (CDH) was recrystallised from methanol.

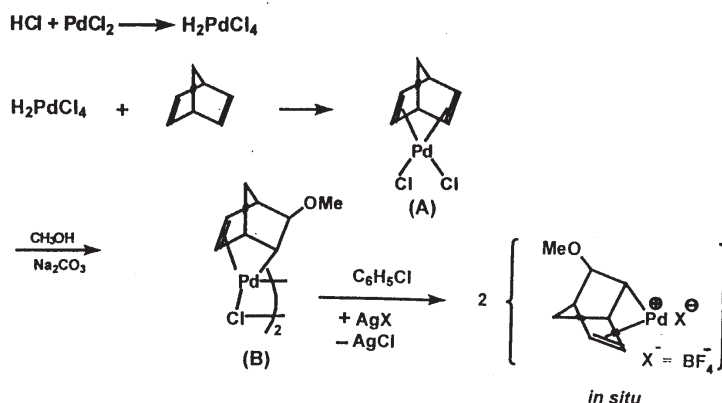
Exo-norbornene 2,3-dicarboxyanhydride (nadic anhydride) was prepared from commercially available nadic anhydride by thermal isomerisation according to the procedure of Castner and Calderon [4].

N-aryl nadimides were prepared by reacting *o*-toluidine/*m*-toluidine/*p*-toluidine with exo-nadic anhydride using glacial acetic acid as solvent. Details of synthesis of N-tolyl nadimides have been described elsewhere [9]. The melting point of N-*o*-tolyl (N-1), N-*m*-tolyl (N-2) and N-*p*-tolyl (N-3) nadimides were found to be 156, 134 and 192°C, respectively.

Synthesis of Pd(II) catalyst

Bicyclo [2.2.1] heptadiene palladium chloride was prepared as described by Drew and Doyle [17]. PdCl₂ (2.0 g) was dissolved in conc. HCl (5 mL) by stirring at 150°C for 1 h. The brown solution obtained was cooled to room temperature and diluted with ethanol (150 mL) and filtered. Norbornadiene (2.5 mL) was added to the filtrate with stirring. The yellow product precipitated was filtered and washed with diethyl ether. It was recrystallised from dichloromethane and dried at room temperature under vacuum. A yellow solid with 77% yield was obtained.

Analysis for C₇H₈PdCl₂ (A): found C 31.6%, H 2.96%, Calculated C 31.20%, H 2.99%. IR (KBr) ν_{max} 3041 (s, C–H stretch of olefinic bond), 1638 (w, C=C stretch), 1450 (s, CH₂ scissoring), 1404 (s, C–H bending), 1304 (s), 1226 (s), 1181 (s), 1158



Scheme 2 Reaction scheme for synthesis of Pd(II) catalyst

(s) (CH_2 twisting and wagging), 1087 (m), 1047 (m), 967 (s), 897 (s), 828 (m), 788 (s), 768 (s) (out of plane C–H bending) cm^{-1} (s, m and w denote sharp, medium and weak absorptions, respectively).

$^1\text{H-NMR}$ ($\text{DMSO-}d_6$) : δ 1.89 (t, 2H, CH_2), 3.57 (q, 2H, bridge head protons), 6.76 (t, 4H, olefinic protons) ppm.

Di μ chloro-bis-(6-methoxybicyclo [2.2.1] hept-2-ene-endo-5 σ .2 π) palladium(II) (B) was synthesized by addition of Na_2CO_3 and methanol, to the yellow product obtained according to the method by Green and Hancock [18].

In the $^1\text{H-NMR}$ spectrum (CDCl_3) of (II) the signals at δ 6.06 (t, 1H), 5.86 (m, 1H) (vinylic protons), 4.12 (q, 1H, CHPd), 3.22 (s, 3H, CHOCH_3), 3.16 (m, 1H, CHOCH_3), 2.78 (m, 2H, CH_2), 1.9 (m, 1H, CH, bridge head proton), 1.58 (m, 1H, CH, bridge head proton α to OMe) were observed.

Polymerization

For a monomer/catalyst mole ratio of 100, a mixture of palladium chloride dimer (16.5 mg, 0.062 mmol) and AgBF_4 (19.5 mg, 8.1 mmol) were weighed in glove box in a round bottom flask and chlorobenzene was injected into it.

The contents were stirred for 15 min at room temperature under nitrogen atmosphere. The solution of the yellow catalyst was filtered to remove AgCl and the filtrate was added to the nadimide solution (0.24 mol L^{-1}) in chlorobenzene at room temperature and then allowed to stir for 36 h. The solution was precipitated in methanol, filtered and dried. The grey polymer thus obtained was purified by stirring it with silica gel in dichloromethane for 24 h. It was filtered and the polymer was precipitated in methanol. The polymer was separated, washed with methanol and then dried under vacuum. The other polymerization were performed similarly. The polymers obtained from N-1, N-2 and N-3 have been designated as AN-1, AN-2 and AN-3, respectively.

Characterization

Vibrational spectra of monomers and polymers was recorded in KBr pellets using Biorad Digilab FTS-40 spectrophotometer. ^1H and $^{13}\text{C-NMR}$ spectra were recorded in CDCl_3 using tetramethylsilane as an internal standard and a Jeol JNM-FX 100 FT NMR spectrometer. Gel Permeation Chromatography (GPC) was performed on a 0.2 g dL^{-1} polymer solution in CHCl_3 . Two $10 \mu\text{m}$ polymer mixed gel columns ($600 \times 8 \text{ mm}$), polystyrene standards and a differential spectrometer as detector and a pump from Knauer were used.

Thermal stability was assessed in nitrogen atmosphere by a thermobalance TG 50 and a thermoanalytic processor Mettler TA 3000. A nitrogen flow rate of $60 \text{ cm}^3 \text{ min}^{-1}$, a heating rate of $10^\circ\text{C min}^{-1}$ and a sample size of $10 \pm 2 \text{ mg}$ was used.

Results

Characterization of polymers

In the FTIR spectra of these polymers, besides the absorption bands due to the carbonyl group of the imide at 1778 and 1708 cm^{-1} , the peaks due to 1,2-, 1,3- and 1,4-disubstituted benzene were observed at 751 , 774 and 809 cm^{-1} for AN-1, AN-2 and AN-3, respectively. The sharp absorption bands due to out-of-plane C–H bending vibrations present in the monomers in the range $650\text{--}1000\text{ cm}^{-1}$ disappeared in the polymers (Fig. 1).

In $^1\text{H-NMR}$ spectrum of the polymers (Fig. 2) the signal due to olefinic protons at 6.28 ppm disappeared which confirmed formation of a saturated polymer. The aromatic protons appeared as a multiplet around 6.7 to 7.5 ppm . The methyl protons were located at 2.25 ppm for AN-3 and AN-2 but at 2.1 ppm for AN-1 which could be attributed to the shielding effect of the methyl substituent at *ortho* position. A multiplet was observed due to the two methylene protons around 1.17 ppm and the allylic and the methine protons showed a complex signal from 3.6 to 2.8 ppm .

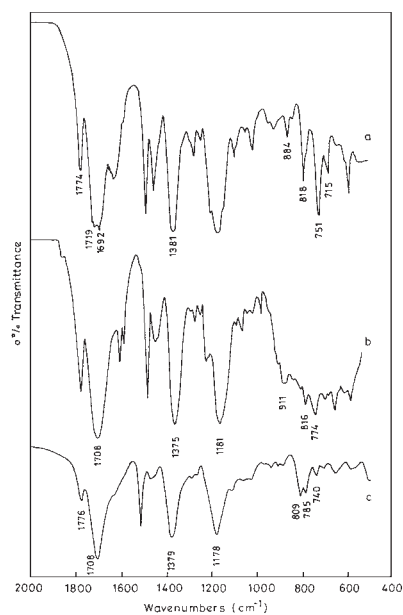


Fig. 1 FTIR spectra of a) AN-1, b) AN-2, c) AN-3

The $^{13}\text{C-NMR}$ spectrum of PN-3 showed a signal due to carbonyl carbon at 177 ppm . The aromatic protons were magnetically non-equivalent and were observed at 138 , 129.6 , 129 and 125.6 ppm . The methyl carbon signal was located at 21.17 ppm and the carbons at positions 5-, 6-, 1,4- and 2,3- appeared as a multiplet in the range 49.7 to 29.7 ppm . The carbon at C-7 was observed at 30.3 ppm (Fig. 3).

Under similar conditions of polymerization AN-2 showed higher \overline{M}_n (33490) than AN-3 (24240) or AN-1 (10130) (Table 1).

Table 1 Effect of substituent on % yield and molecular mass

| Sample designation | Yield/% | $\overline{M}_n/\text{g mol}^{-1}$ | $\overline{M}_w/\text{g mol}^{-1}$ | PDI |
|--------------------|---------|------------------------------------|------------------------------------|------|
| AN-1 | 28 | 10134 | 14911 | 1.47 |
| AN-2 | 53 | 33487 | 48429 | 1.44 |
| AN-3 | 86 | 24244 | 40170 | 1.65 |

The thermogravimetric traces of poly (*N*-*o*-/*m*-/*p*-tolyl nadimides) are shown in Fig. 4. A 1–4% mass loss was observed in the temperature range of 200–250°C. Similar mass loss was observed in polymers prepared by ROMP and was attributed to loss of solvent [9]. A reverse Diels Alder reaction leading to loss of cyclopentadiene from end groups in nadimides has been reported above 200°C [19–20]. Therefore the observed mass loss above 200°C in the present polymers can be attributed to these processes. The major mass loss was observed above 400°C. The temperatures of (a) initial mass loss (T_i), (b) maximum rate of mass loss (T_{\max}) and final decomposition temperature (T_f) were noted from these traces and are reported in Table 2. Presence of methyl substituent at *o*-, *m*- or *p*-position in the benzene ring only marginally affected the characteristic decomposition temperatures of the polymers. However char yield at 800°C was highest in AN-2 while for AN-1 and AN-3 it was comparable.

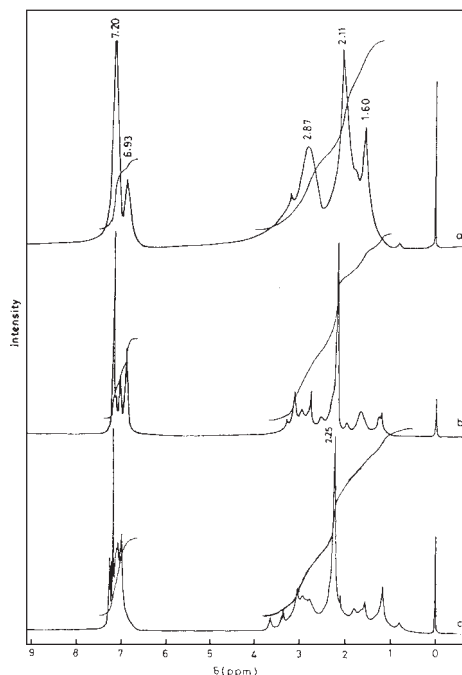


Fig. 2 $^1\text{H-NMR}$ spectra of a) AN-1, b) AN-2, c) AN-3 in CDCl_3

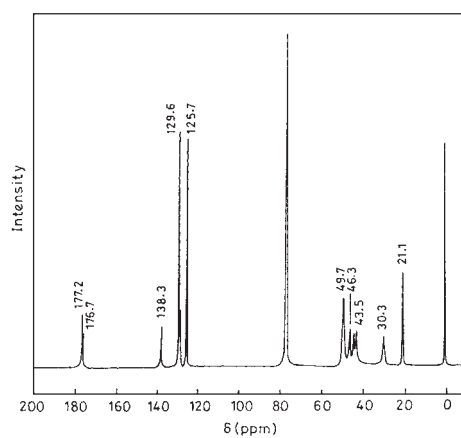


Fig. 3 ^{13}C -NMR spectra of AN-3 in CDCl_3

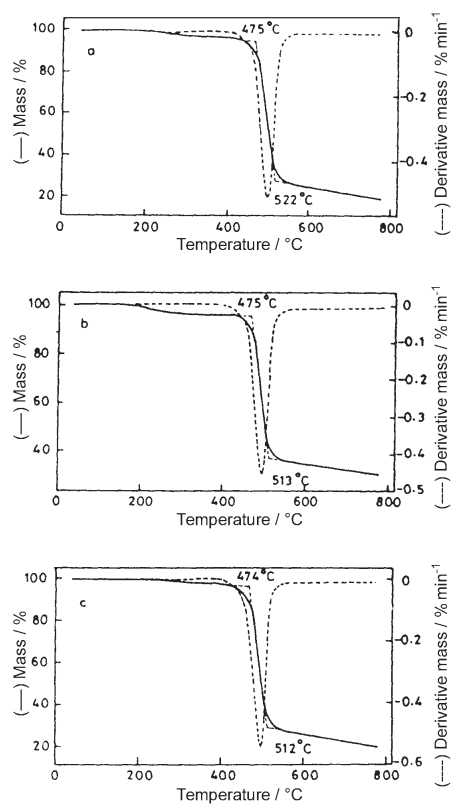


Fig. 4 TG/DTG traces of a) AN-1, b) AN-2, c) AN-3 in nitrogen atmosphere (heating rate: $10^\circ\text{C min}^{-1}$)

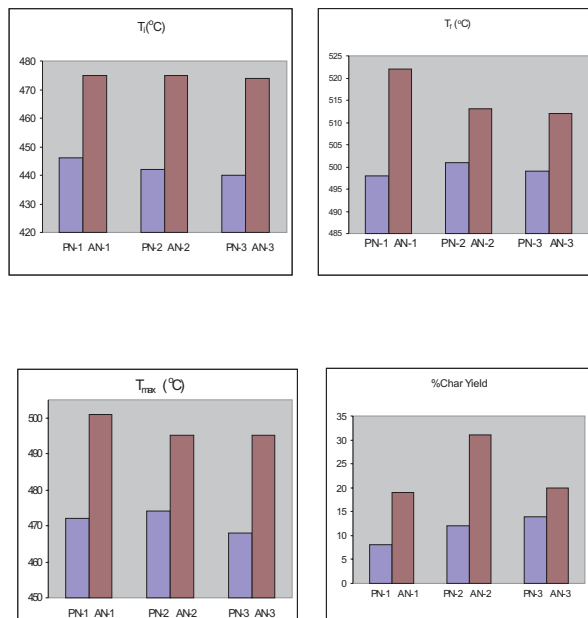


Fig. 5 Comparison of thermal characteristics of polymers derived from N-aryl nadimide by ROMP and carbocationic polymerization

The polymers derived from carbocationic polymerization showed higher thermal stability in comparison to those derived from ROMP. The T_i , T_f and T_{max} values for AN-1, AN-2 and AN-3 were higher by 25–30°C in comparison to polymers prepared by ROMP. The % char yield was also found to be higher (19–31%) for these polymers compared to ROMP polymers (8–14%). These differences in thermal behaviour are obvious from Fig. 5.

Table 2 Results of thermogravimetric analysis of polymers derived by carbocationic polymerization

| Sample designation | T_i /°C | T_{max} /°C | T_f /°C | Char yield at 800°C/% |
|--------------------|-----------|---------------|-----------|-----------------------|
| AN-1 | 475 | 501 | 522 | 19 |
| AN-2 | 475 | 495 | 513 | 31 |
| AN-3 | 474 | 495 | 512 | 20 |

It can, therefore, be concluded that presence of bicyclo ring in the backbone increases thermal stability significantly in comparison to polymers having unsaturation.

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