High-Temperature Metathesis Polymers: Structure–Property Relationships

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ABSTRACT: This paper describes the synthesis of *N*-phenylnorbornene-5,6-dicarboximides (NDIs) with substituents at different positions in the aromatic ring and their polymerization by ring-opening metathesis polymerization (ROMP) leading to high-temperature polymers. A structure–property relationship study showed that the polymer properties are significantly influenced by the size and position of the substituent groups on the ring. Substitution at the ortho position leads to an increase in the glass transition temperature (T_g) of the polymer, whereas meta substitution has the opposite effect. An increase in the size of the substituent for ortho-substituted polymers is found to further increase the T_g. Polymers with T_gs up to 270 °C are prepared by choosing an appropriate substituent at the ortho position. It is proposed that changes in the polymer properties, observed when the size and/or position of the substituent is changed, are due to the differences in the relative ease of segmental motion of the polymer backbone. Molecular modeling studies suggest that the barrier to rotation of the phenyl group is at a maximum when the substituent is at the ortho position. In addition, resistance to rotation increases with the increase in the size of the substituent. Phenyl rotation is not significantly affected when the substituent is at the meta or the para position. Blends of poly(*N*-phenylnorbornenedicarboximide) with ortho and meta substituents are found to immiscible, giving two distinct T_gs corresponding to the T_gs of the homopolymers. Copolymerization of the ortho- and meta-substituted NDIs results in a homogeneous random copolymer with one glass transition temperature. The glass transition temperature increases linearly as the amount of ortho-substituted phenyl content in the copolymer increases.

Introduction

Ring-opening metathesis polymerization (ROMP) of norbornenedicarboximides with aliphatic and aromatic substituents has been described in the literature.[1–5] We recently reported the polymerization behavior of the exo and endo isomers of *N*-phenylnorbornenedicarboximide.[1] The exo isomer was found to polymerize into a high molecular weight straight-chain polymer with interesting thermal and thermochemical properties; polymerization of the endo isomer led only to the oligomers in low conversions. Melt rheological behavior and the physical and mechanical properties of injection-molded poly(*exo*-*N*-phenylnorbornenedicarboximide) have been investigated, and a heat distortion temperature in excess of 170 °C was reported.[2]

In-situ metathesis polymerization of *N*-phenylnorbornenedicarboximide with unsaturated rubber leads to rubber grafted PNDI, which shows a very good balance of high heat and impact properties.[2] Invention of the living metathesis catalyst for the polymerization of substituted norbornenes, including imides, by Schrock et al.[3,6–8] opens many interesting possibilities for the synthesis of polymers with novel properties.

Properties of the polymers prepared by ROMP of substituted norbornene can be varied substantially by simply changing the substituent group or the stereochemistry of the substituent group on the norbornene.[9–11] This paper describes novel polymers of *N*-phenylnorbornenedicarboximides with different substituents at the ortho, meta, and para positions. The effect of substituents on the properties of the monomer, its polymerization, and polymer properties is described.

Experimental Section

exo-Norbornene-5,6-dicarboxylic anhydride (*exo*-NDA), was prepared by the thermal isomerization of the corresponding endo isomer as described by Kastner and Calderon.[12] Aniline, substituted anilines, diethylaluminum chloride, tungsten hexachloride, and acetaldehyde diethyl acetal, which was distilled before use, were purchased from Aldrich Chemical Co.

Synthesis of *N*-(*o*-Bromophenyl)norbornenedicarboximide. To a 500-mL round-bottom flask equipped with a mechanical stirrer, a condenser, a thermo-watch, and a dropping funnel were added 93.7 g (0.57 mol) of norbornenedicarboxylic anhydride and 100 mL of MEK. At room temperature, 99.3 g (0.58 mol) of *o*-bromoaniline dissolved in 75 mL of MEK was added to this mixture by the dropping funnel. The anhydride and bromoaniline did not react at room temperature for an hour. The temperature was raised and the reaction was carried out at reflux for another hour. The reaction mixture on analysis showed mainly the presence of the starting materials. The reaction mixture was then divided into two portions. To one part was added 1.0 g of trimethylamine and to the other part 1.0 g of *p*-toluenesulfonic acid. Both parts were refluxed and reacted for ~1 h to give a quantitative yield of the amic acid. The amic acid from both portions was combined and added to a 500-mL round-bottom flask followed by 6.0 g of sodium acetate and 125 mL of acetic anhydride. The reaction was carried out at reflux for 2 h. The clear solution of the imide formed after the reflux was cooled and then precipitated in water. The product was recrystallized using a mixture of acetone and water. The melting point was found to be 199–202 °C. ^1H and ^{13}C chemical shifts are given in Table 1.

Synthesis of *N*-(*m*-Bromophenyl)norbornenedicarboximide. The reaction was carried out in exactly the same manner as described in the previous section except that the addition of triethylamine or the *p*-toluenesulfonic acid was not required for the synthesis of the amic acid. The melting point of the product after recrystallization was 181–184 °C. ^1H and ^{13}C chemical shifts are given in Table 1.

Catalyst Preparation. In a typical example 0.5634 g of tungsten hexachloride was dissolved in 2.8 mL of toluene, and to this partly dissolved WCl_6 was added 0.4 mL of acetaldehyde diethyl acetal. A reaction between WCl_6 and acetal takes place with the release of HCl, and a burgundy colored solution is obtained. Nitrogen is passed through this solution overnight to remove the HCl.

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Table 1

(a) ^1H Chemical Shifts (ppm) of *N*-Phenyl-*exo*-norbornene-5,6-dicarboximides with Substituents at the Ortho, Meta, and Para Positions

substituent	H2 + H3	H1 + H4	H5 + H6	H7a, H7b	shift diff between H7a and H7b
o-F	6.350	3.209; 3.209	2.974; 2.883	1.476	0.0
m-F	6.350	3.196	2.845	1.443	0.0
p-F	6.350	3.194	2.837	1.450; 1.426	0.024
o-Cl	6.350	3.242; 3.215	2.995; 2.870	1.778; 1.488 1.508	0.290
m-Cl	6.350	3.197	2.843	1.45	0.000
p-Cl	6.350	3.195	2.841	1.449; 1.419 1.428	0.030
o-Br	6.350	3.246; 3.214	2.986; 2.861	1.931; 1.490 1.51	0.441
m-Br	6.350	3.196	2.838	1.451	0.000
p-Br	6.350	3.192	2.84	1.448; 1.412 1.422	0.036
m-I		3.182	2.818	1.444	

(b) ^{13}C Chemical Shifts (ppm) of *N*-Phenyl-*exo*-norbornen-5,6-dicarboximides with Substituents at the Ortho, Meta, and Para Positions

substituent	carbonyl		olefin	C5,6	C7	C1,4
o-F	major	176.19	137.58	47.88	44.88	42.39
	minor			47.52	45.09	42.70
	diff			0.36	−0.21	−0.32
m-F	1.76.45		137.83	47.60	45.00	42.78
p-F	176.71		137.77	47.52	44.93	42.70
o-Cl	major	175.98	137.79	48.15	44.61	42.87
	minor		137.73	47.43	45.14	42.74
	diff			0.72	−0.53	0.13
m-Cl	176.43		137.81	47.63	44.56	42.79
p-Cl	176.52		137.77	47.58	44.95	42.71
o-Br	major	175.88	137.82	48.20	44.56	43.22
	minor	172.53	137.78	47.41	45.14	42.73
	diff			0.79	−0.58	0.49
m-Br	176.42		137.80	47.63	44.95	42.79
p-Br	176.49		137.79	47.60	44.95	42.72
m-I	176.47		137.79	47.62	44.93	42.79

Table 2. Effect of Phenyl Substitution on the Conversion, Structure, Molecular Weight, and Molecular Weight Distribution of Poly(*N*-phenyl-*exo*-norbornene-5,6-dicarboximide)

substituent	conv (%)	cis (%)	M_n (kg/mol)	M_w (kg/mol)	MWD
unsubstituted	99.0	40	24.2	53.2	2.2
o-F	92.5		29.0	765.1	26.5
m-F	95.0	40	24.5	71.8	2.9
p-F	100	43	12.0	54.1	4.5
o-Cl	100	39	31.3	107.0	3.4
m-Cl	97.5	40	15.1	47.5	3.1
p-Cl	92.5	43	14.0	33.0	2.5
o-Br		35			
m-Br	85.0	41	26.3	75.8	2.9
p-Br	90.0	3.3	15.1	48.6	3.3

Polymerization. Polymerization was carried out by dissolving 2.0 g of the desired norbornenimide in 4 mL of 1,2-dichloroethane. To the monomer solution was added 0.1 mL of the catalyst solution (0.5 M tungsten hexachloride in toluene) followed by 0.17 mL of diethylaluminum chloride (2.05 M solution in heptane). The polymerization was carried out at 60 °C for 2 h. Polymer was isolated by precipitation of the reaction mixture in methanol. The precipitated polymer was again dissolved in methylene chloride and reprecipitated in methanol, filtered, and dried in a vacuum oven at 60 °C overnight. The molecular weight, as measured by SEC using chloroform as a solvent, and the yields of the different polymers are reported in Table 2.

Polymer Characterization. Molecular Characterization. One-dimensional ^1H and ^{13}C NMR spectra were recorded at 25 °C with a Varian VXR 300 spectrometer operating at ^1H and ^{13}C frequencies of 300 and 75 MHz, respectively. The spectrometer was equipped with a four-nucleus 5-mm probe purchased from Nalorac and an automatic sample changer. The spectra were acquired and processed with Varian/Monsanto MNMR software residing on a Sun computer. Typical acquisition conditions were as follows: ^1H spectra, 30° pulse (5.4 μs), 6600-Hz sweep, 30 400 data points zero-filled to 65 536, 2.3-s delay between pulses; ^{13}C spectra, 30° pulse (4.6 μs), 18 762-Hz sweep, 56 320 data points zero-filled to 65 536, 1.5-s delay between pulses. The ^1H and ^{13}C spectra were referenced to the DMSO-d_6 solvent peak at 2.49 and 39.5 ppm, respectively.

Molecular weight and molecular weight distributions were measured by size exclusion chromatography. Polystyrene standards were used as a reference. Measurements were done at 35 °C using Waters Ultrastyragel columns of mean permeability of 100, 500, 10^3, 10^4, and 10^6 Å connected to a Waters differential refractive index (DRI) detector. Chloroform was used as the mobile phase, and the flow rate was 0.5 mL/min.

Glass transition temperatures were measured on a Perkin-Elmer DSC-2. The samples were encapsulated in standard aluminum DSC pans in duplicate. Each pan was run twice. Samples were heated from 30 to 300 °C in a nitrogen atmosphere at a rate of 20 °C/min. The T_g was calculated using the alternate T_g method on the HP1000/LMS system for all samples. This method defines the midpoint of the total change in heat capacity as the T_g. All calculations were done on the second heat. Pure indium metal standard was used to calculate the temperature correction factor. Correcting factors were used in the software for all samples.

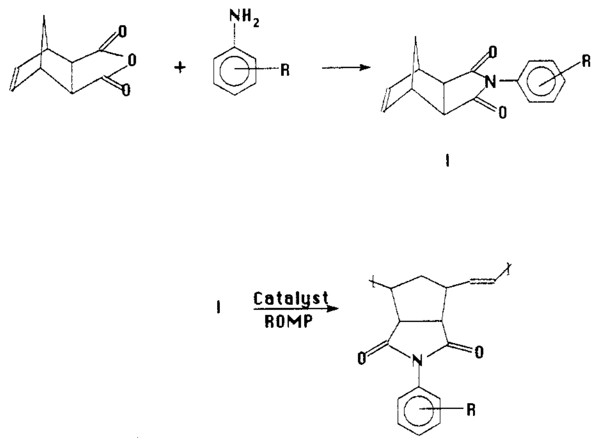
Dynamic mechanical analysis (DMA) traces were generated on a Rheometrics RSA-II instrument. The temperature was varied at a rate of 3 °C/min. Storage (E') and loss (E'') moduli vs temperature were measured from which tan δ (E'/E'') was plotted.

Results and Discussion

Monomer Synthesis. Aniline reacted readily with *exo*-norbornene-5,6-dicarboxylic anhydride to give the corresponding amic acid, which was cyclized to *N*-phenyl-*exo*-norbornene-5,6-dicarboximide either by thermal dehydration or by the use of a dehydrating agent like acetic anhydride. The reactivity of the substituted aniline was found to depend on the type of substituent and its position relative to the amine group. When the aniline is substituted with electron-withdrawing halogen groups, the nucleophilicity and hence the reactivity toward the anhydride were reduced. It was observed that *o*-bromoaniline did not react with the anhydride under the same conditions in which aniline was highly reactive. The reaction could, however, be carried out if either the anhydride or the aniline was activated by the use of an acidic or a basic catalyst. A quantitative yield of the amic acid was obtained when the *o*-bromoaniline/exo-NDA reaction was catalyzed either by *p*-toluenesulfonic acid or by triethylamine. The deactivating effect of the cyano substituent was so high that even in the presence of a catalyst, the *o*-cyanoaniline did not react with norbornenedicarboxylic anhydride. Contrary to the ortho-substituted aniline, *m*-bromo- or *m*-cyanoaniline reacted readily with the anhydride, without any need of a catalyst, to give the corresponding amic acid. Monomers after crystallization were characterized by ^1H and ^{13}C NMR. The ^1H chemical shifts can be found in Table 1a. Although H1,H4 and H5,H6 are magnetically equivalent and appear as broad triplets and singlets, respectively, when the aromatic ring is ortho substituted, each peak appears twice. The peaks are generally shifted downfield from the position of the meta- and para-substituted compounds.

Ortho and para substitution with halogen (F to Br) caused increasing separation of H7a and H7b with bulkiness. H7a and H7b were found to be magnetically equivalent for meta-substituted monomers.

Scheme 1



^{13}C chemical shifts of the aliphatic carbons are reported in Table 1b. The meta- and para-substituted *N*-phenylnorbornenedicarboximides gave expected ^{13}C chemical shifts but again ortho substitution led to two inequivalent C1, C4, C5,6, and C7 carbons. A possible explanation for these observations is that the ortho-substituted phenyl ring assumes two preferred and distinct orientations which do not disturb the symmetry of the norbornene molecule—i.e., the plane of the aromatic ring must be in the plane of symmetry of norbornene: in one orientation the ortho substituent is pointed up, in the other down. Raising the temperature to 55 °C was not sufficient to bring about a change in the ^{1}H spectrum.

Polymer Synthesis: Effect of the Size and Position of the Substituent. *N*-Phenylnorbornenedicarboximides with substituents at the ortho, meta, and para positions were metathetically polymerized in an effort to understand the effect of the phenyl substitution on the polymerization behavior and polymer properties. The ring-opening metathesis polymerization was carried out using tungsten hexachloride as a catalyst and diethylaluminum chloride as an activator. Toluene or 1,2-dichloroethane was used as a solvent.

N-Phenylnorbornenedicarboximides with substituents like fluoro, chloro, and bromo were investigated for polymerization. All monomers used in the polymerization were of exo stereochemistry. No special effort was made to achieve the highest molecular weight. Total conversion was determined by analyzing the reaction mixture by size exclusion chromatography (SEC). In some cases the total conversion was based on the polymer yield. After the removal of the residual monomers, polymers were characterized for the microstructure by NMR and the molecular weight and molecular weight distribution by SEC. ^{1}H NMR was used to determine the cis/trans content in the polymer. Cis ^{1}H appeared at higher field, 5.46 ppm, compared to trans ^{1}H, which appeared at ~5.69 ppm. The cis contents in the polymers are shown in Table 2. As reported for other polymers prepared using a tungsten-based catalyst system, the cis content in the polymers ranged from 33 to 43%.[10] Substituent group and its position on the phenyl ring did not play a significant role on the resulting stereochemistry of the double bonds in the polymer. Table 2 also shows the SEC data for polymers substituted with F, Cl, and Br groups. Para-substituted polymers are invariably of lower molecular weight, and this is probably due to the poor solubility of the para-substituted monomers and polymers. Changing the substituents on the phenyl ring did not significantly affect the conversion; the polymer yield remained above 85% irrespective of the substituent. However, NDI containing an ortho iodo substituent did not polymerize.

Table 3. Effect of Phenyl Substitution on the T_g of Poly(*N*-phenyl-*exo*-norbornene-5,6-dicarboximide)

substituent	ortho substituent	T_g (°C) meta substituent	para substituent
H	220	220	220
F	239	208	225
Cl	256	205	226.3
Br	270	200	227.8
I		199	

The substituent on the phenyl ring, irrespective of its position and size, did not significantly affect the conversion, the molecular weight, and the stereochemistry of the resulting double bond in the polymer. Since all polymers are fairly high molecular weight with very similar contents of cis and trans double bonds (S = 0.33–0.43), any difference in the properties of the polymers is anticipated to be due to the size and the position of the substituent group on the phenyl ring.

Thermal and Thermomechanical Properties of Poly(*N*-phenyl-*exo*-norbornene-5,6-dicarboximide) Containing Different Substituents on the Phenyl Ring. The thermal properties of poly(*N*-phenyl-*exo*-norbornene-5,6-dicarboximides) containing different substituents on the phenyl ring were investigated by DSC. Dynamic mechanical properties were measured with a Rheovibron at a constant frequency of 11 Hz. Polymers were soluble in chlorinated solvents from which clear and tough films could be cast. These films were used for the dynamic mechanical measurements.

The glass transition temperatures for the ortho-, meta-, and para-substituted polymers as measured by DSC are given in Table 3. All the ortho-substituted polymers show higher T_gs compared to the unsubstituted polymer. A significant dependence of the T_g on the size of the substituent is also observed. The T_g increases with the increase in the size (van der Waals radius (VDR)) of the ortho substituent. Among PNDI with ortho halo substitution, the bromo-substituted polymer has the highest T_g.

These results appear to suggest that the reasons responsible for the high T_g are mainly steric. Making the substituent at the ortho position bulkier results in increased hindered rotation of the phenyl group.

Molecular modeling studies were carried out to study the rotation about the C–N bond for the PNDI containing different substituents at the ortho, meta, and para positions. Each structure was built and then minimized with the MMX force field.[13,14] The relative energy was then calculated as a function of the dihedral angle. A rigid rotor approximation was used; i.e., the structure was not reminimized for each angle. Figure 1 shows the model for the repeat unit of the polymer from *N*-(*o*-chlorophenyl)-*exo*-norbornene-5,6-dicarboximide.

Figure 2 shows the strain energy plotted against the dihedral angle for PNDI with H, F, Cl, and Br substituents at the ortho position. The maximum barrier to rotation is observed at the dihedral angles of 0 and 180°. The barrier to rotation is minimum for phenyl and maximum for *o*-bromophenyl, increasing with an increase in the size of the ortho substituent. The T_g increases nearly linearly as the barrier to rotation of the phenyl group increases (Figure 3).

The barrier to rotation of the phenyl ring at the C–N bond is not affected when the substituents are at the para position and very little effect is observed for meta-substituted PNDI. The strain energy for unsubstituted

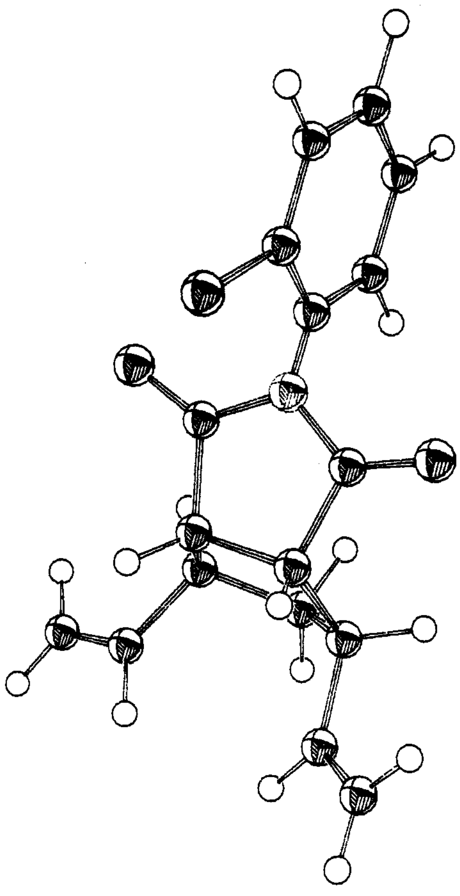


Figure 1. Poly(*N*-(*o*-chlorophenyl)-*exo*-norbornene-5,6-dicarboximide).

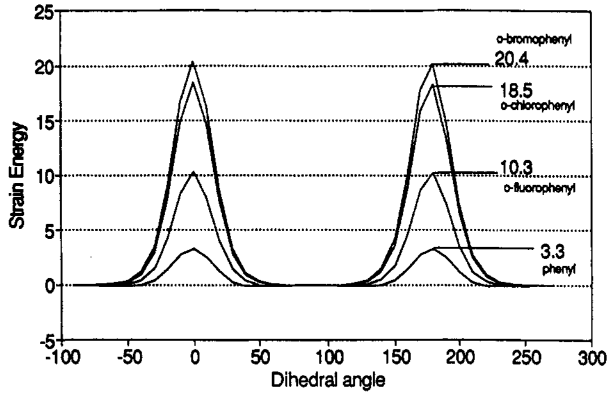


Figure 2. Strain energy vs dihedral angle for ortho-substituted PNDIs.

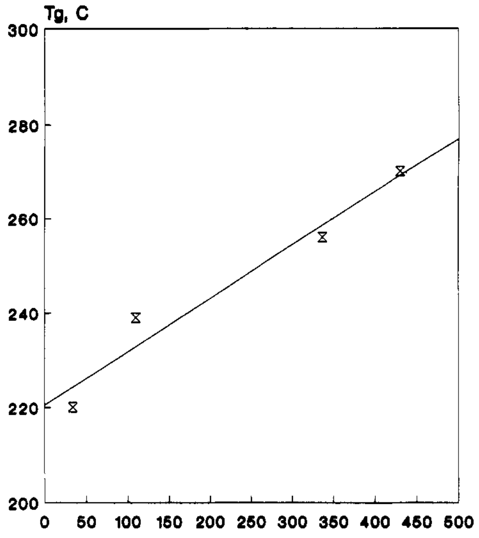


Figure 3. Correlation between barrier to phenyl rotation and T_g (°C).

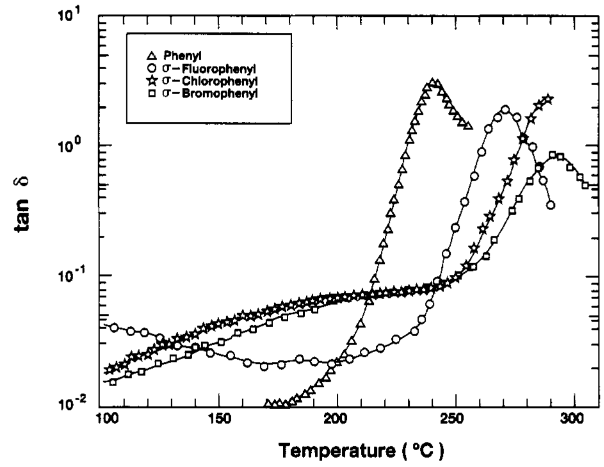


Figure 4. tan δ vs temperature for ortho-substituted PNDIs.

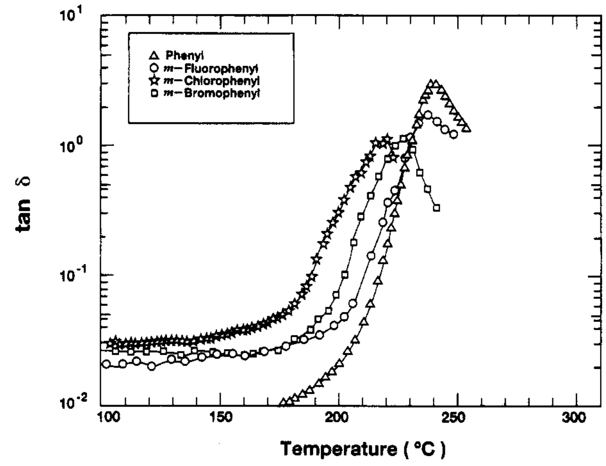


Figure 5. tan δ vs temperature for meta-substituted PNDIs.

or meta/para-substituted PNDI is in the range 3.1–3.4. As shown in Table 3, for PNDI with F, Cl, Br, and I substituents at the meta position, the glass transition temperature decreases with an increase in the size of the substituent, although the effect is not as pronounced as for ortho-substituted polymers. The decrease in the T_g for PNDI with the bulky substituent at the meta position is probably due to increased separation of the macromolecular chains, resulting in increased free volume and relative ease in segmental motion.

Dynamic mechanical properties of PNDI and substituted PNDI were investigated on solution-cast films. Loss tangent as a function of temperature for polymers with ortho-substituted phenyls is shown in Figure 4. The α-dispersion peaks, tan δ_{max}, for ortho-substituted polymers are significantly higher compared to that for unsubstituted PNDI and move to higher temperatures with an increase in the size of the ortho substituent. These results, similar to those of the DSC and molecular modeling, indicate that the ortho substitution leads to restriction in the segmental motion. The loss tangent vs temperature for PNDI and meta-substituted PNDIs is plotted in Figure 5. The maximum in the tan δ occurs at lower temperatures for the meta-substituted polymers compared to the unsubstituted polymer. The dynamic modulus vs temperature plots for the ortho- and meta-substituted polymers are shown in Figures 6 and 7, respectively. The dynamic modulus of the unsubstituted

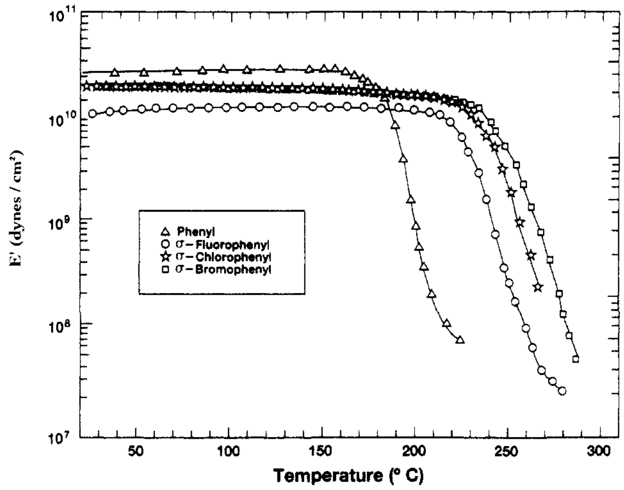


Figure 6. Dynamic modulus vs temperature for ortho-substituted PNDIs.

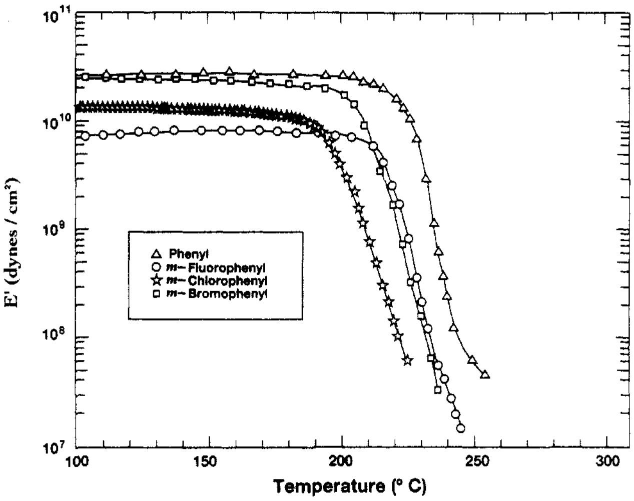


Figure 7. Dynamic modulus vs temperature for meta-substituted PNDIs.

PNDI is also plotted for comparison. The drop in the dynamic modulus is observed at much higher temperatures for the ortho-substituted polymer compared to the unsubstituted PNDI, and as expected from the T_g and tan δ plots, the bulkier the ortho substituent, the higher the temperature at which the modulus shows a drop. The meta-substituted polymers show a completely different behavior; the drop in the dynamic modulus is observed at lower temperatures compared to the unsubstituted PNDI.

Structure–Property Relationship of the Polymers and the Copolymers of NDI with Different Substituents on the Phenyl Ring. Three different sets of copolymers with different amounts of ortho and meta halo substituents were synthesized: (1) copolymers of ortho- and meta-fluoro NDIs, (2) copolymers of ortho- and meta-chloro NDIs, and (3) copolymers of ortho- and meta-bromo NDIs.

Polymers containing different amounts of ortho and meta substituents were prepared by dissolving appropriate amounts of the two monomers in a solvent and then carrying out the polymerization using a tungsten/aluminum alkyl catalyst system. Quantitative yields of the homo- and copolymers are obtained irrespective of the type of substituent. Table 4–6 show the conversion for the polymerization of NDIs containing different amounts of fluoro, chloro, and bromo substituents.

DSC thermograms for all the copolymers show change in the specific heat only at one temperature, indicating that random copolymers are formed. Formation of random copolymers is also supported by the fact that ortho- and meta-substituted homopolymers are not miscible. Figure 8 shows the DSC thermograms of the *o*-Cl-PNDI, *m*-Cl-PNDI, and a 50/50 mixture of the two homopolymers. The blend was prepared by dissolving *o*-Cl-PNDI and *m*-Cl-PNDI in methylene chloride, a good solvent for both components, and then evaporating the solvent. The thermogram of the blend shows two distinct T_gs nearly at exactly the same temperature as the homopolymers, indicating total immiscibility. Copolymers at all compositions gave only one T_g. The T_g values of the copolymers are in between the T_g values of the two homopolymers, and the T_g increases with the increase in the content of ortho-substituted imides. Figure 9 shows the plot of glass transition temperature vs the ortho content in the

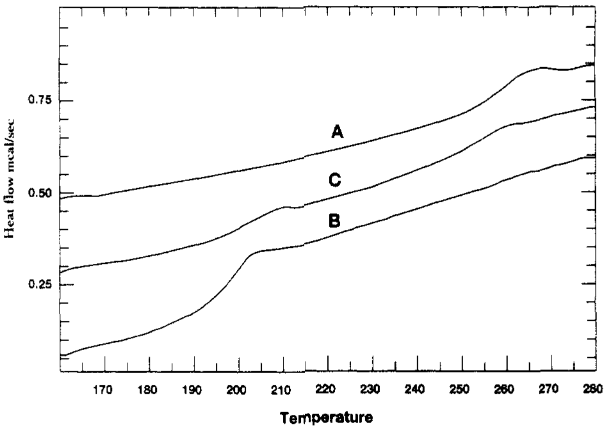


Figure 8. DSC thermogram of (A) *o*-Cl-PNDI, (B) *m*-Cl-PNDI, and (C) blend of A and B prepared in solution.

Table 4. Copolymers of *N*-(*o*-Fluorophenyl)- and *N*-(*m*-Fluorophenyl)-*exo*-norbornene-5,6-dicarboximides: Effect of Polymer Composition on the Properties

o/*m*	conv (%)	T_g (°C)	tan δ_{max} (°C)
100/0	80	238.9	261
80/20	90	232.5	257
60/40	85	225.1	247
40/60	97.5	218.7	242
20/80	90.0	213.1	234
0/100	90.0	207.8	229

Table 5. Copolymers of *N*-(*o*-Chlorophenyl)- and *N*-(*m*-Chlorophenyl)-*exo*-norbornene-5,6-dicarboximides: Effect of Polymer Composition on the Properties

o/*m* comp	conv (%)	T_g (°C)	tan δ_{max} (°C)
100/0	92.5	255.6	290
90/10	92.5	259.2	
80/20	95.0	249.2	275
70/30	87.5	241.2	
60/40	95.0	237.7	265
50/50	80.0	226.3	
40/60	95.0	222.3	245
30/70	97.5	216.3	
20/80	90.0	211.6	235
10/90	90.0	206.6	
0/100	92.5	204.8	220

Table 6. Copolymers of *N*-(*o*-Bromophenyl)- and *N*-(*m*-Bromophenyl)-*exo*-norbornene-5,6-dicarboximides: Effect of Polymer Composition on Polymer Properties

o/*m*	conv (%)	T_g (°C)	tan δ_{max} (°C)
100/0	97.5	270.2	291
80/20	97.5	255.8	285
60/40	90.0	229.6	261
40/60	80.0	229.6	251
20/80	82	214.7	237
0/100	85	203.5	224

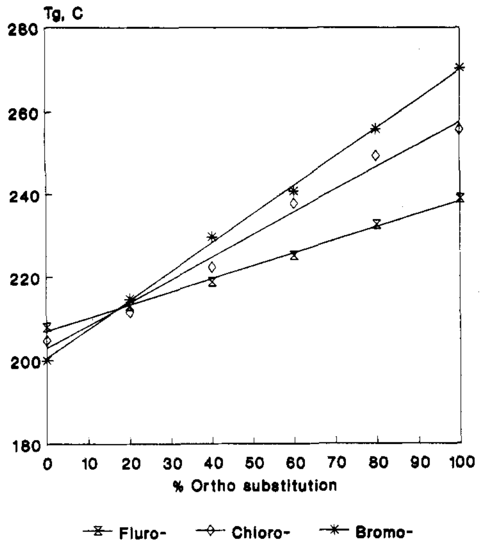


Figure 9. T_g vs the ortho content in the ortho/meta copolymers of PNDI.

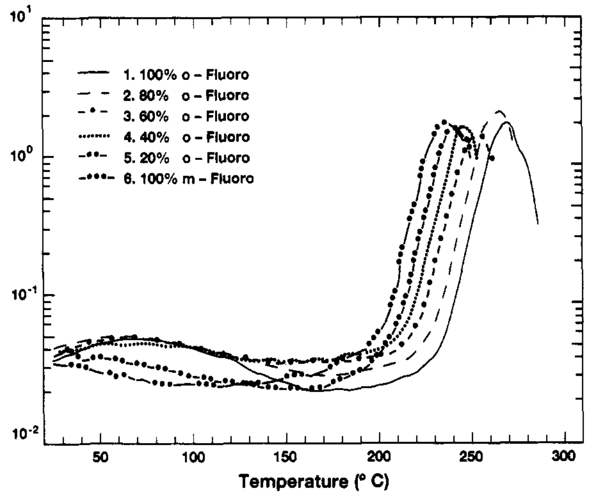


Figure 10. tan δ vs temperature for homo- and copolymers of NDI with ortho- and meta-fluoro substituents.

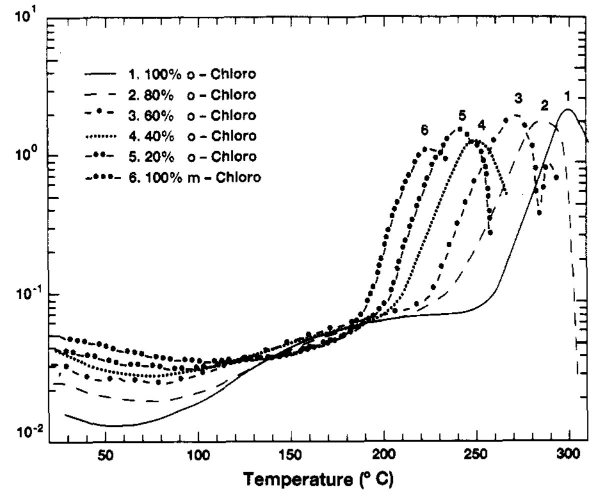


Figure 11. tan δ vs temperature for homo- and copolymers of NDI with ortho- and meta-chloro substituents.

copolymers. As can be seen, T_g increases linearly with the increase in the ortho imide content. The effect of the polymer composition on the T_g is more pronounced for bromo-substituted polymer and least for the fluoro-substituted polymer, again indicating that the size of the substituent is very important.

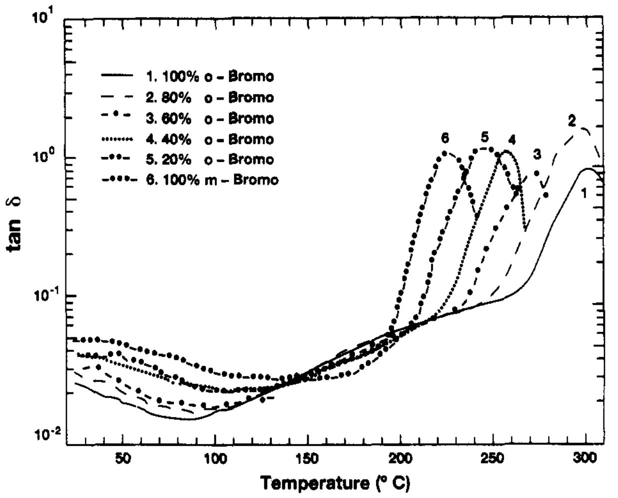


Figure 12. tan δ vs temperature for homo- and copolymers of NDI with ortho- and meta-bromo substituents.

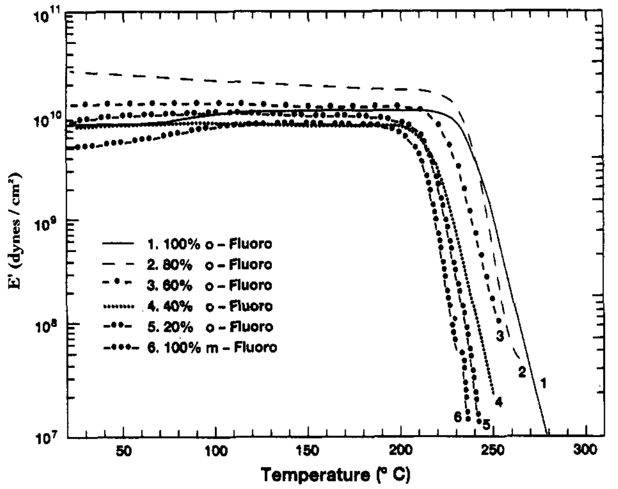


Figure 13. Dynamic modulus vs temperature for homo- and copolymers of NDI with ortho- and meta-fluoro substituents.

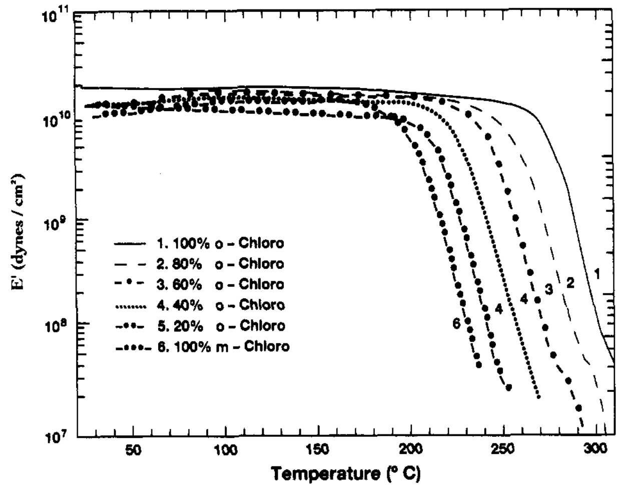


Figure 14. Dynamic modulus vs temperature for homo- and copolymers of NDI with ortho- and meta-chloro substituents.

Dynamic mechanical properties of the copolymers were investigated on solution-cast films. All copolymers studied showed only one α-dispersion peak, indicating that there are no separate phases of ortho and meta PNDI and the copolymers formed are random giving a single-phase system. tan δ_{max} shifts to higher temperatures as the amount of ortho NDI increases in the copolymer, and the increase in the tan δ_{max} is linear just like the increase in the T_g measured by DSC (Figures 10–12).

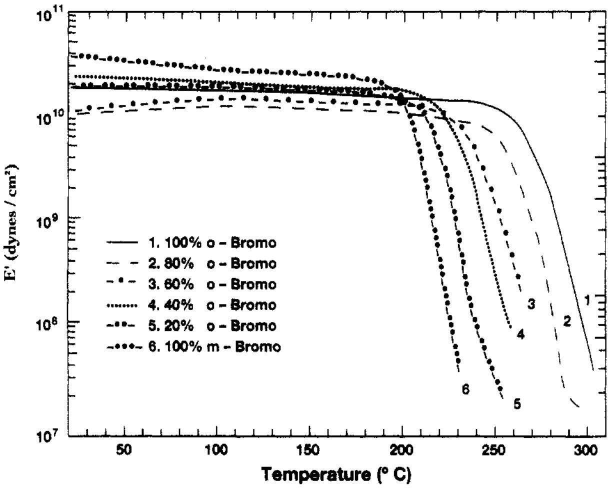


Figure 15. Dynamic modulus vs temperature for homo- and copolymers of NDI with ortho- and meta-bromo substituents.

Dynamic modulus vs temperature plots for the homopolymers and the copolymers of ortho- and meta-substituted PNDI are shown in Figures 13–15. As the concentration of ortho-substituted imide groups in the copolymer increases, the drop in the modulus takes place at comparatively higher temperature. The effect is more pronounced for the bulkier bromo substituent.

Conclusion

Metathesis polymerization of *N*-phenylnorbornenedicarboximide (NDI) and substituted NDI produces amorphous materials with high glass transition temperatures. Properties of these polymers can be tailored easily by appropriate substitution of the phenyl group in NDI and also by copolymerization. Physical blends of the homopolymers of NDI with the same substituent at different positions in the phenyl ring are found to be incompatible, giving two distinct T_gs. Copolymers of NDI with substituents at the ortho and meta positions are found to be random when produced using the WCl_6-based catalyst system; copolymers have a single T_g which increases linearly with the increase of the ortho substituent.

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