Synthesis, Rheology, and Physical Properties of a Metathesis Polymer

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SYNOPSIS

This paper describes the synthesis, physical properties, and the impact modification of poly(*N*-phenylnorbornene dicarboximide) (PNDI). Impact modification is carried out both by physical blending with acrylonitrile–butadiene rubber (Hycar®) and by *in situ* metathesis polymerization of the monomer with the rubber. Better success is achieved by *in situ* metathesis polymerization. A copolymer, poly(*N*-phenylnorbornene dicarboximide)-*co*-poly(norbornene nitrile) containing Hycar rubber (PNDI/PNN/Hycar), is prepared with a good balance of high-heat impact and flexural properties. The melt viscoelastic behavior of PNDI/PNN/Hycar is evaluated and the energy of activation for viscous flow (E_a) was found to be 42 kcal/mol. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Ring-opening metathesis polymerization (ROMP), where cyclic olefins are converted to straight-chain polymers in the presence of a suitable catalyst, is a very versatile reaction. Polymers ranging in properties from soft rubber to hard and tough thermoplastics and cross-linked thermosets can be prepared by this chemistry.[1-7] ROMP of strained cycloolefin is relatively fast and exothermic and has considerable tolerance for the polar functionalities attached to the cycloolefins. Consequently, polymers of norbornene with ester,[3] acetate,[4,5] nitrile,[6-8] carbonate,[9,10] anhydride,[11,12] and imide[13-15] functionalities have been reported.

ROMP of norbornene nitrile and the properties of poly(norbornene nitrile) have been investigated in great detail.[6-8] Most of the reports of norbornene with polar functionalities have, however, been limited to the polymerization aspect of the monomer. Information about the rheology and physical and mechanical properties of polynorbornene with a polar substituent is not available.

This article describes the synthesis, rheology, and physical/mechanical properties of poly(*N*-phenylnorbornene dicarboximide) (PNDI) and its copolymers with norbornene nitrile. Impact modification of PNDI with a butadiene–acrylonitrile rubber, Hycar®, is described. Copolymerization with norbornene nitrile in the presence of Hycar provides a polymer with a good balance of properties.

EXPERIMENTAL

Tungsten hexachloride, acetal, diethylaluminum chloride, and 5-norbornene-2-carbonitrile (NN) were purchased from Aldrich Chemical Co. Hycar-1042 was received from B. F. Goodrich. Ethanox® and Polygard® were purchased from Ethyl Corp. and Uniroyal, respectively. NN was distilled before use. The isomer ratio in NN, as analyzed by ^{13}C NMR, was found to be 55/45 *exo*/*endo*.

The *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.[8] *Exo*-*N*-Phenyl norbornene dicarboximide (*exo*-NDI) was prepared from the *exo*-NDA and the aniline as described previously.[12]

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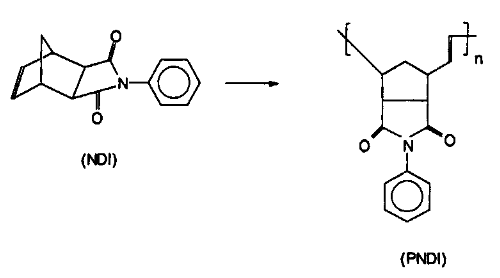
Synthesis of Poly(exo-*N*-phenyl norbornene dicarboximide) (PNDI)

To a solution of 3.45 g of NDI in 21 mL of 1,2-dichloroethane was added 0.15 mL of 0.5*M* tungsten hexachloride/acetal solution in toluene (mol ratio of WCl_6/acetal was 1/2) followed by 0.22 mL of 2.05*M* diethylaluminum chloride in heptane. The reaction was carried out at 65°C for 4 h. The polymer was precipitated in methanol. The precipitated polymer was dissolved in methylene chloride and reprecipitated in methanol, filtered, and dried in a vacuum oven at 60°C overnight. The inherent viscosity, as measured in chloroform, was 1.03 dL/g.

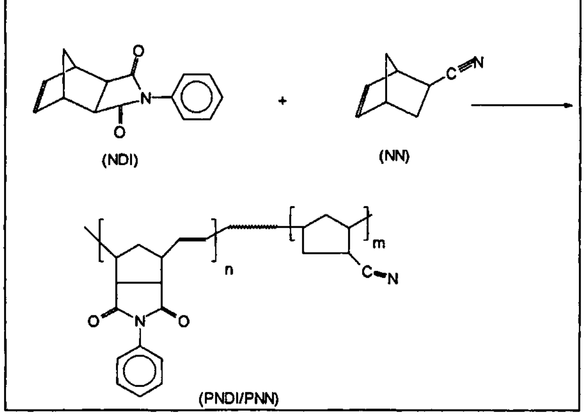
Synthesis of Rubber-modified Poly(*N*-phenyl norbornene dicarboximide) (PNDI/Hycar)

Hycar-1042, 7.0 g, was dissolved in 250 mL of 1,2-dichloroethane. To this solution was added 55.0 g of NDI. WCl_6/acetal, 2.3 mL (0.5*M* in toluene) was then added, followed by 2.9 mL of Et_2AlCl solution (2.05*M* in heptane). The reaction was carried out at 65°C for 4 h. The polymer was recovered in the same manner as was PNDI.

Scheme 1



Scheme 2



Synthesis of rubber-modified poly(*N*-phenyl norbornene dicarboximide)-*co*-poly(norbornene nitrile) (PNDI/PNN/Hycar)

Hycar-1042, 14 g, was dissolved in 300 mL of 1,2-dichloroethane in a reaction kettle. Sixty grams of *exo*-NDI and 40 g NN were added to the kettle while stirring. To this mixture was then added 5.4 mL WCl_6/acetal solution (0.5*M* in toluene) followed by 6.6 mL of Et_2AlCl. Reaction was carried out at 65°C for 4 h. The product was recovered in the same manner as was PNDI.

RESULTS AND DISCUSSION

ROMP of *exo*-NDI using a tungsten-based catalyst system results in straight-chain PNDI of high molecular weight with high conversions.[13] The polymerization medium is heterogeneous in the beginning due to poor solubility of the monomer, but as the reaction proceeds, a clear and homogeneous solution is formed. The polymer is recovered by precipitation in methanol. The unsaturation in the polymer, as measured by proton NMR, was 60% *trans* and the glass transition temperature, as measured by DSC, was 227°C.

The polymer, recovered by precipitating the solution in methanol, was fibrous and an attempt to extrude the polymer was unsuccessful. In an effort to densify the system, the polymer solution produced during the polymerization was subjected to vacuum distillation in order to remove the solvent. Polymer was then cut and chopped in the Thomas mill and dried in a vacuum oven at 100°C for 18 h. The polymer has such a high affinity for the chlorinated solvents that a temperature higher than the T_g of the polymer is needed to remove the last traces of the solvent. It was found that Thomas milled polymer, when refluxed with methanol, filtered, and dried, was suitable for extrusion. Polymer was extruded on a twin-screw extruder and then injection-molded on an Arburg-100. Physical properties of PNDI homopolymer are listed in Table I, column I.

PNDI is a high-heat, high-strength, high-modulus polymer. Impact strength, however, is too low for many applications. Impact modification of the polymer was carried out by blending it with rubber. A blend of PNDI with Hycar-1042 rubber was made in a twin-screw extruder. The ratio of the matrix polymer to the rubber was 9 : 1. The extrusion temperature used was 280°C. Properties of the rubber-modified polymer is listed in Table I, Column II. As can be seen, the impact is significantly improved

Table I Properties of Poly(*N*-phenylnorbornene dicarboximide) (PNDI)

	I	II
Tensile		
Strength (Pa)	6.0×10^7	5.9×10^7
Modulus (Pa)	2.8×10^9	2.4×10^9
Elongation (%)	1.4	5.3
Flexural		
Flex. strength (Pa)	8.8×10^7	6.2×10^7
Flex. modulus (KgCm^2)	2.9×10^9	2.4×10^9
Impact		
Izod (notched) (J/M)	18.6	53.4, 90.7[a]
Heat deflection temp (°C)		
At 1.82×10^6 (Pa)	191	171

I = PNDI; II = PNDI and Hycar rubber (10%) physical blend.

[a] PNDI and Hycar *in situ* metathesis.

(53.4 J/m from 18.6 J/m) but it is still not attractive enough for many applications.

Impact Modification by *In Situ* Metathesis Polymerization with the Rubber

Impact modification of PNDI by physical blending with rubber, as described in the previous section, has been only partly successful. In an effort to further improve the impact strength of the polymer, NDI was polymerized in the presence of Hycar rubber.

Hycar was dissolved in 1,2-dichloroethane along with the monomer, which was then polymerized using a metathesis catalyst. Antioxidants present in Hycar were removed prior to polymerization by precipitating a 10% toluene solution of Hycar in methanol. Removal of antioxidants was performed to prevent possible deactivation of the catalyst. Ethanox, antioxidant, and Polygard were then added after the polymerization was complete.

In the process described above, grafting of PNDI onto the rubber is expected because of the presence of double bonds in the rubber. The nature of bonding between the rubber and PNDI has not been investigated, but it is very likely that the rubber is incorporated in the polymer chain as blocks rather than as true grafts as obtained in addition-type polymerization between the monomer and the rubber. Metathesis degradation of polybutadiene, where double bonds of the polybutadiene participate in the metathesis reaction to give oligomeric polybutadiene, has been well documented.[16] Metathesis degradation of unsaturated polymers has been successfully used for the investigation of the sequence distribution of different copolymers,[17] including the butadiene–acrylonitrile copolymer.[18] The degradation yield is found to be strongly dependent on the acrylonitrile content of the copolymer. Incorporation of Hycar into PNDI by this mechanism will result in blocks of relatively shorter segments of the elastomer in the final copolymer.

Polymer prepared by *in situ* metathesis polymerization with rubber had an Izod impact of 90.7 J/m compared to 53.4 J/m when rubber was blended with PNDI. Better impact properties of rubber-modified polymer, prepared by *in situ* metathesis polymerization of Hycar and NDI, is probably due to the bonding between the PNDI and the rubber arising from cross-metathesis. A preliminary investigation of rubber-modified polymer by electron microscopy has shown that the size of the rubber particles in the physically blended system is higher than in the rubber-grafted polymer. The rubber phase is also more agglomerated in the case of the physically blended system than that of the grafted polymer.

Since *in situ* metathesis polymerization of NDI and Hycar was relatively successful, we decided to synthesize a copolymer of NDI with norbornene nitrile by *in situ* metathesis polymerization of these monomers on Hycar. The choice of norbornene nitrile as a comonomer was made because the polymers produced from monosubstituted norbornene are relatively less rigid than are the polynorbornenes with bridgehead substitution like PNDI[6,13] and, therefore, easier to impact modify. The presence of nitrile in the copolymer may also be desirable for better adhesion with the rubber phase, which also contains the nitrile groups. The copolymer PNDI/PNN/Hycar was, therefore, synthesized. The ratio of NDI/NN/Hycar was 52/35/13. Copolymerization of NDI and NN leading to a random copolymer has previously been reported.[13] The PNDI/PNN/Hycar reported here was investigated by DSC and the dynamic mechanical analysis. Figure 1 shows the dynamic modulus, loss modulus, and tan delta vs. temperature plot for PNDI/PNN/Hycar. Only one maximum in E'' (180°C) and the tan delta (191°C) is observed, indicating that a random copolymer is formed; similarly, the drop in the dynamic modulus is also observed at one temperature. Figure 2 shows the DSC thermogram of PNDI/PNN/Hycar. The major change in specific heat is observed

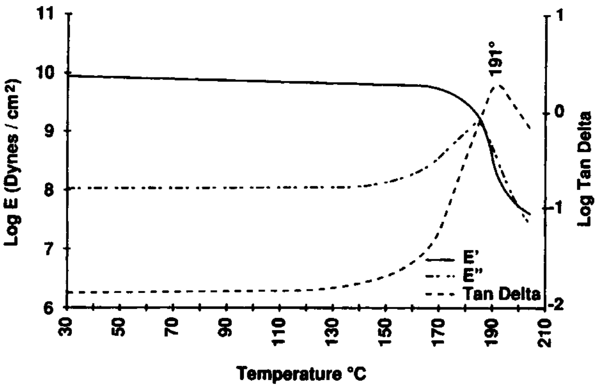


Figure 1 Dynamic mechanical properties of PNDI/PNN/Hycar as a function of temperature.

primarily at 171°C, again indicating the random copolymer nature of this polymer. The DSC thermogram (Fig. 2) does show a slight change in the specific heat at 225°C, which is very close to the T_g of the PNDI, so possible formation of random blocks is not excluded. Further investigation will be carried out to resolve this issue.

The polymer was extruded and molded at 260°C. Physical properties of the injection-molded samples are listed in Table II. Good balance of heat distortion, impact strength, and flexural properties is achieved. The copolymer has good ductility with 31.5% elongation to break. The data clearly indicate that a polymer with good balance properties can be prepared by *in situ* metathesis polymerization.

This polymer was further characterized by its melt rheological behavior. The viscoelastic melt of the PNDI/PNN/Hycar melt was compared with the commercial acrylonitrile–butadiene–styrene (ABS) copolymer.

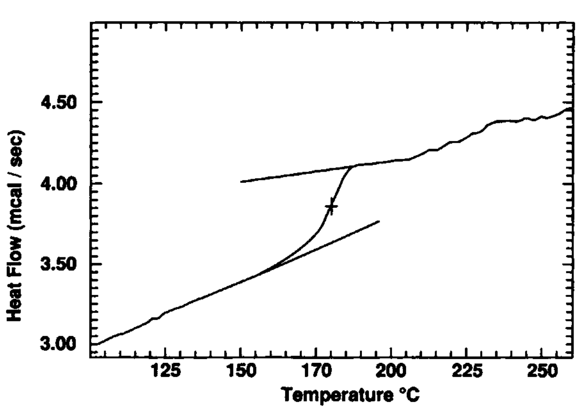


Figure 2 DSC thermogram of PNDI/PNN/Hycar.

Table II Properties of PNDI/PNN/Hycar

Tensile	
Strength (Pa)	5.2×10^7
Modulus (Pa)	1.9×10^9
Elongation (%)	31.5
Flexural	
Flex. strength (Pa)	7.8×10^7
Flex. modulus (Pa)	2.1×10^9
Impact	
Izod (notched) (J/M)	416.3
Heat deflection temp (°C)	
At 1.82×10^6 (Pa)	138

PNDI/PNN/Hycar = (52/35/13).

Rheological Characterization of PNDI/PNN/Hycar

The melt viscosity of PNDI/PNN/Hycar was measured as a function of shear rate, temperature, and time. The material was tested on a Rheometrics mechanical spectrometer (RMS) in the oscillatory shear, parallel plate mode from 0.01 to 100 rad/s at 250, 260, 274, 288, and 300°C.

Viscosity vs. shear rate curves for PNDI/PNN/Hycar, at the five temperatures, can be seen in Figure 3. The η^* curves at 250, 260 and 274°C look normal (i.e., well separated, no crossovers), whereas at 288°C,the η^* curve is about equal to 250°C from

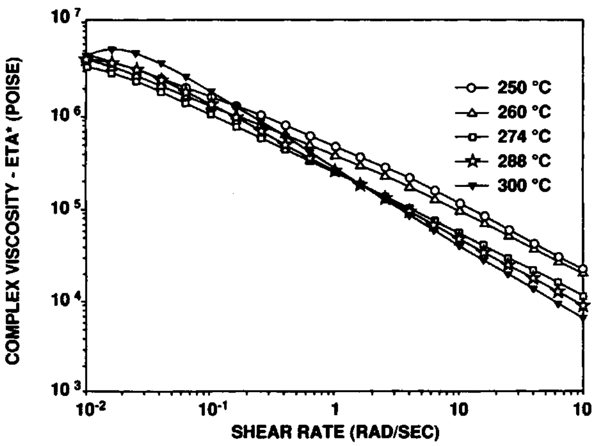


Figure 3 Viscosity vs. shear rate for PNDI/PNN/Hycar.

0.01 to 0.04 rad/s, crossing over the 260°C curve at 0.1 rad/s and the 274°C curve at 1 rad/s. The 300°C η^* curve is well above the curves for the other temperatures at 0.01 to 0.1 rad/s, crossing over 250°C at 0.1 rad/s, 260°C at 0.4 rad/s, and both 274 and 288°C at 4.0 rad/s. All the curves are well separated at shear rates above 10 rad/s. The general features of the shear modulus curves (Fig. 4) at the five temperatures are essentially the same as the viscosity curves with the same crossovers as noted earlier. The apparently elevated viscosities and shear moduli at the lower shear rates at 288 and 300°C are possibly the result of network formation within the polymer melt that is eventually broken up at higher shear rates.

The T_g of this material, 191°C as obtained from the DMA (Fig. 1), is about 60°C below the lowest melt viscosity measurement temperature (250°C), indicating that the material should be well within the melt region at all five test temperatures. We can calculate the energy of activation (E_a) for viscous flow using the Arrhenius relationship

$$\ln a_T = \frac{E_a}{RT} - \ln B$$

where a_T is the shift factor for superposition and R is the universal gas constant. The complex viscosity, η^*, and shear rate were determined from the intercept of a line representing a constant shear stress (τ) with the η^* curves for the five temperatures. The ln a_T values were then plotted vs. $1/T$ and a linear least-squares fit applied to the curve resulting in an equation of the same form as that of the Arrhenius relationship (Fig. 5). The energy of activation for PNDI/PNN/Hycar was determined to be 42.3 kcal/mol using this method.

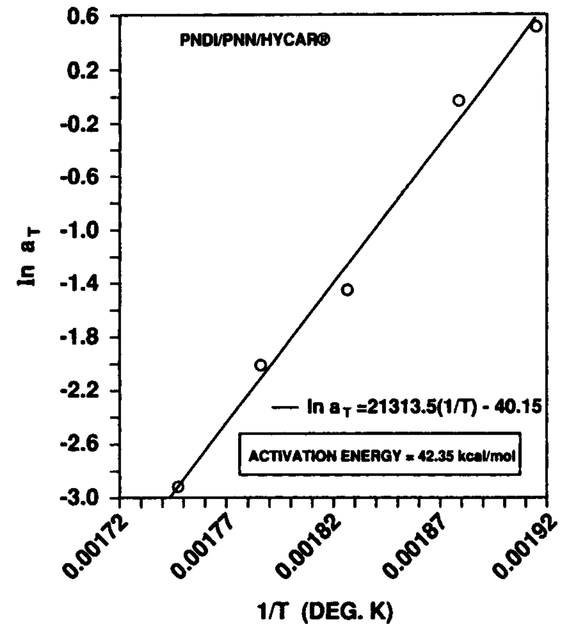


Figure 5 Shift factor ln a_T vs. inverse temperature for PNDI/PNN/Hycar.

Figure 6 shows viscosity vs. shear rate curves for PNDI/PNN/Hycar at 250 and 260°C and a standard acrylonitrile–butadiene–styrene copolymer (ABS), Monsanto LN452, (E_a = 25 kcal/mol) at 200 and 225°C. The viscosity curve for PNDI/PNN/Hycar at 250°C matches up well with that of ABS at 200°C at higher shear rates (> 10 rad/s),

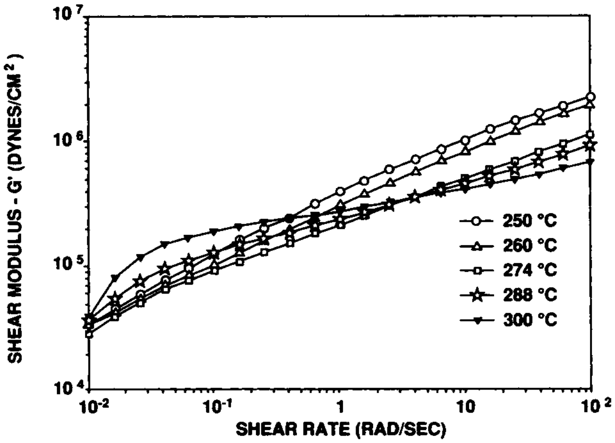


Figure 4 Shear modulus vs. shear rate for PNDI/PNN/Hycar.

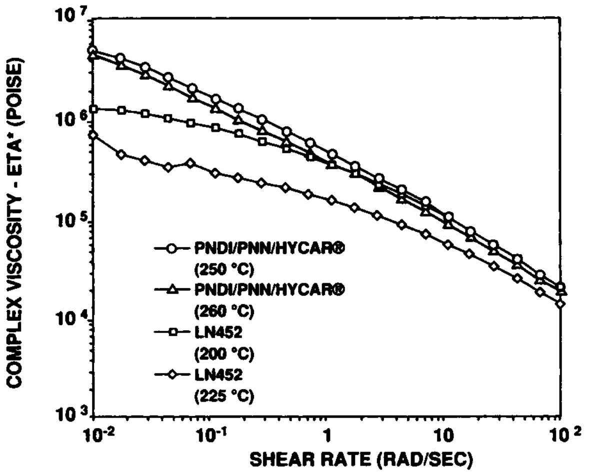


Figure 6 Viscosity vs. shear rate for PNDI/PNN/Hycar and LN 452 (ABS).

but at lower shear rates, the viscosity curves begin to diverge significantly with PNDI/PNN/Hycar, exhibiting a greater shear rate dependence than that of ABS.

CONCLUSION

Polymerization of *exo*-NDI results in a high-strength, high-modulus polymer with high glass transition temperature (227°C). The impact strength is low. Rubber toughening of PNDI and PNDI/PNN copolymers is carried out by different methods, including *in situ* metathesis polymerization of the monomers in the presence of rubber. Rubber grafting is expected in this process. It is shown that the *in situ* metathesis reaction with the rubber is more effective, resulting in better impact strength than from blending. Impact-modified polymers with a good balance of heat distortion and impact were prepared.

The melt viscosity behavior of Hycar-modified PNDI/PNN copolymer is measured as a function of shear rate, temperature, and time and compared with the ABS copolymer. The energy of activation for viscous flow is found to be 42 kcal/mol compared to 25 kcal/mol for ABS.

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