

Reaction Injection Molding (RIM) System Based on Metathesis

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SYNOPSIS

This paper describes the polymerization and the copolymerization of dicyclopentadiene and norbornene nitrile by metathesis polymerization. It is found that the metathesis polymerization of dicyclopentadiene, which is very fast and exothermic, can be controlled by the addition of norbornene nitrile. Though the norbornene nitrile delays the polymerization at room temperature, at high temperatures, because of the presence of nitrile group, polymerization is accomplished in reaction injection molding time. Physical and mechanical properties of the polymers and copolymers are described. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Reaction injection molding (RIM), a process where a reactive mixture of monomers or oligomers is polymerized in a mold to produce the finished product, has been dominated by urethane chemistry.¹ Ring opening polymerization, in general, can meet most requirements of a RIM process. Fast reaction, low to moderate heat of polymerization, and no by-products of polymerization are the main attributes of the ring-opening polymerization.² Anionic and metathesis ring-opening reactions have, therefore, been successfully used to produce nylon^{3,4} and polydicyclopentadiene⁵⁻⁹ parts, respectively.

Application of metathesis polymerization to the RIM process was first described in 1983,⁷ where the dicyclopentadiene polymerization was described as producing highly crosslinked polydicyclopentadiene with excellent properties, by RIM process.

Reaction injection molding of cycloolefins uses a two-component catalyst system, with a transition metal-salt catalyst such as WCl_6 in conjunction with aluminum alkyl as an activator. One component consists of catalyst solution in the monomer and the other component consists of the activator solution in a second monomer stream. These two components are mixed in the mixing head of a RIM machine during injection of the reactive mixture into the

mold. The reactive mixture polymerizes into the shaped article in the mold.

This paper describes the modification of metathetically polymerizable nonpolar cycloolefins (which are very fast and sometimes unmanageable) into RIM system. Modification is achieved by using small amounts of functionally substituted cycloolefins having electron-rich substituents such as nitrile, ester, and acetate. Because these groups are attached to metathetically polymerizable monomers, the modifier not only delays but also participates in the polymerization. The properties of the polymers, so produced, are also described.

EXPERIMENTAL

Dicyclopentadiene and 5-norbornene-2-carbonitrile (NN) were purchased from Aldrich Chemical Co. and were freshly distilled before use. Dicyclopentadiene, used for the polymerization was mainly endo isomer. The NN was a mixture of 55% exo and 45% endo isomers.

Activator/monomer solution was prepared by mixing neat diethyl aluminum chloride with dicyclopentadiene.

Catalyst Preparation

Catalyst solution is first prepared in toluene and then mixed with the monomer. In a typical example,

0.5635 g of tungsten hexachloride is mixed with 2.8 mL of toluene and 0.4 mL of acetal is added to the partly dissolved solution of WCl_6 . A reaction between WCl_6 and acetal takes place with release of HCl and a burgundy-colored solution is obtained. Nitrogen is passed through this solution overnight to take out HCl and then it is diluted with the norbornene nitrile to a desired molarity.

Polymerization

Polymerization was carried out by mixing a solution of the activator in dicyclopentadiene and the catalyst was prepared as a solution in norbornene nitrile.

For the temperature rise studies, the reactive mixture was injected into a vial containing a thermocouple in the center, at 100°C. Although efforts were made to minimize the heat loss, true adiabatic conditions were not achieved.

For evaluation of polymer properties, polymerization was conducted in a mold. Activator and catalyst solutions, prepared separately in dicyclopentadiene and norbornene nitrile, were mixed in a small reaction bomb inside a glove box in an inert atmosphere at room temperature. The reactive mixture was injected into the mold at room temperature by pressurizing the bomb with nitrogen. The mold was then closed on both sides and the polymerization was carried out by placing the mold in an oven at 100°C for 10 min. After 10 min the mold was open and the molded polymer part was removed for the evaluation of physical properties.

The above are not exactly RIM conditions in which the reactive mixture is usually injected into a preheated mold. It is expected that the difference in the reaction conditions will lead to a difference in the kinetics of polymerization.

RESULT AND DISCUSSION

Solubility of the catalyst, in the solvent used, is very critical for developing a RIM system. It is desirable to minimize the solvent as much as possible because in a RIM system excess volatile solvent will create voids in molded parts and will lead to undesirable effects. Because of the limited solubility of WCl_6 in solvents such as toluene, solutions of high catalyst concentration could not be prepared. Nonreactive solvent, therefore, comprises as much as 3–4% of the RIM system.

We have found that when the catalyst solution is made in toluene, and diethyl acetal of acetaldehyde is used as a modifier, a catalyst solution of 0.5 M can

be made easily. This reduces the amount of toluene in the system to one fourth the amount required in the absence of acetal modifier. This is achieved because the acetal, unlike other modifiers, is a liquid and highly reactive with WCl_6 . When tungsten hexachloride is mixed in toluene and acetal is added to this partially dissolved mixture, there is a very fast sometimes exothermic reaction. The resulting product of this reaction is highly soluble in toluene.

Ring-opening polymerization of cycloolefins, depending on the ring strain, can be a very fast and exothermic process even at room temperature. Therefore, when the catalyst/monomer solution and activator/monomer solution are mixed there is instantaneous polymerization. The polymer sets before the mixture reaches the mold, which creates a problem of mold filling. This extremely fast reaction can be controlled by the use of certain modifiers that will delay the polymerization long enough so that the mold can be filled.⁵

Another important problem is the limited shelf life of the catalyst solution in the monomer. The catalyst polymerizes monomer even without the addition of activator. Although the degree of conversion without addition of activator is not high, the catalyst/monomer solution gels within 30 min. It is postulated that some cationic mechanism is responsible for gelation. The gelation problem can be slowed by the addition of some Lewis base⁵ such as benzonitrile. Because the additives are low molecular weight nonpolymerizable compounds, which are not removed from the system after polymerization (RIM), they cannot be used in large amounts if needed to make the system manageable. Additives used in the polymerization can also diffuse out of the polymer after polymerization, creating a bad surface appearance.

If the functional groups on the modifier responsible for delaying the polymerization are part of a monomer unit that can also take part in the polymerization, then larger amounts of this modifier could be tolerated in modifying the dicyclopentadiene RIM system.

We have modified the dicyclopentadiene RIM system using norbornene nitrile (NN). It was expected that, because of the presence of nitrile functionality, NN will act as a modifier to delay polymerization. But the unsaturation in the norbornene will then participate in metathesis polymerization giving a copolymer of the dicyclopentadiene and the norbornene nitrile.

Polymerization of dicyclopentadiene modified with different amounts of NN was studied by the temperature rise at 100°C. Time for gelation was

Table I Effect of Modifier Concentration on Different Parameters during Reaction Injection Molding of DCPD

Monomer with the Modifier ^a	Room Temperature Polymerization				Polymerization at 100°C	
	T_{max} (°C)	Gel Time (min)	Exotherm Time (min)	Extractables ^b	Exotherm Time (s)	T_{max} (°C)
NN-05	148	2.0	10.0	5.0	30	161, 187
NN-10	148	4.0	14.0	5.8	40	153
NN-20	146	24.5	25.7	7.0	55	191
NN-30	126	25.5	37.0	—	58	171
NN-50	121	40.0	73.0	—	98	164

Reaction conditions: monomer (total) = 63 mmoles; catalyst (WCl_6 /acetal) = 0.37 mmoles (0.6 mol %); Activator (Et_2AlCl) = 0.05 moles (0.08 mol %).

^a Letters denote the modifier and the numbers denote the mol % of the modifier. NN-05 for example is 5 mol % norbornene nitrile and 95 mol % dicyclopentadiene.

^b Extraction was performed in boiling hexane.

monitored visually. Gelation at room temperature gives information about the stability of the catalyst and activator mixed system at room temperature. Time for maximum exotherm at 100°C is the time taken to reach the exotherm after the reactive mixture has been injected in the reaction vessel at 100°C. It can be seen from Table I that the gelation time increases from 2 to 40 min as the NN concentration is increased and reaction time at room temperature (exotherm time) increases from 10 to 73 min.

There is no spontaneous polymerization at room temperature, and the polymerization is delayed enough that the two components can be intimately mixed before they are injected in the mold. Even at NN concentration of 5%, a one component system seems feasible because the stability of the reactive mixture (monomer with catalyst and activator) at room temperature is 1 h. The effect of NN concentration on the polymerization of DCPD at 100°C can be seen in the ATR plots in Figure 1. The time taken for the exothermic reaction increases with the increase in the concentration of NN in the system. As the concentration of NN increases, the exotherm time at 100°C increases from 30 s to a maximum of 98 s, but all the compositions can still be polymerized within the RIM cycle.

Physical Properties of Poly(dicyclopentadiene)-co-poly(norbornene nitrile) (PDCPD/PNN)

For evaluation of physical properties DCPD and NN mixtures were polymerized in the mold. A series of copolymers of DCPD and NN containing 10–100% of NN have been prepared. Polymerization was car-

ried out by injecting under nitrogen a mixture of monomer, catalyst, and activator into a mold that was then sealed and put in an oven at 100°C. After 10 min, molded plaques were removed and analyzed for tensile and impact properties, and Vicat soft-

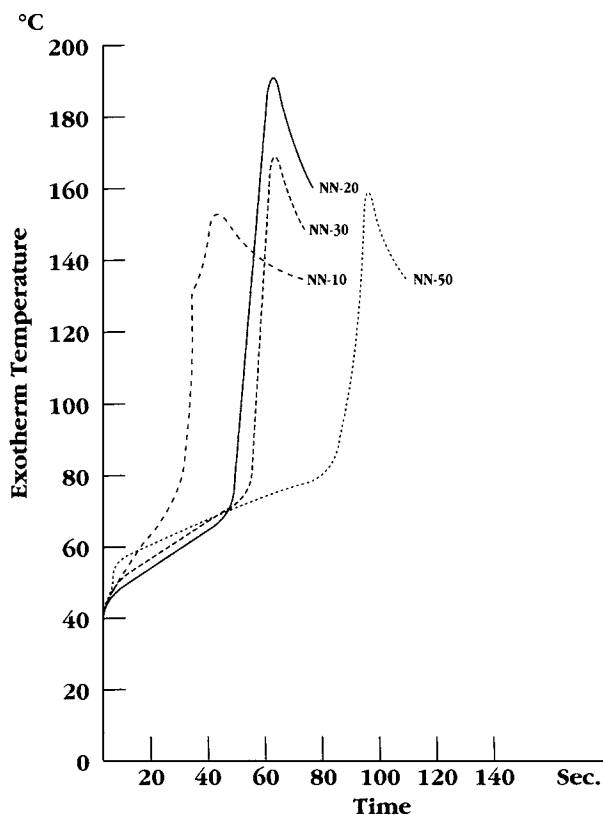


Figure 1 Temperature rise during the copolymerization of dicyclopentadiene and norbornene nitrile.

Table II Properties^a of Polydicyclopentadiene-co-polynorbornene Nitrile

Polymer ^b	Tensile (psi)	% Elong	Modulus ($\times 10^5$ psi)	Notched Izod ft.lb/inch	Vicat Soft Point
PNN 0 ^c	5050	3.4	2.7	2.3	—
PNN 10	5082	2.7	2.34	1.16	60
PNN 20	5864	3.0	2.46	1.05	90
PNN 30	6072	3.7	2.49	1.13	96
PNN 50	4613	3.5	2.45	0.75	65
PNN 60	5473	33.8	2.54	0.67	77
PNN 71	5022	43.6	2.27	0.53	69
PNN 82	6021	45.0	2.70	0.54	71
PNN 100	5552	153.0	2.55	0.48	82
PNN ^d	7400	170	2.7	0.84	—

^a Properties are determined on polymers prepared by injecting the reactive liquid in the mold at room temperature and then increasing its temperature to 100°C.

^b Numbers in PNN-x denote % norbornene nitrile in polydicyclopentadiene-co-polynorbornene nitrile.

^c Kloslewicz.⁵

^d Injection molded PNN.

ening points. Results are shown in Table II. Tensile strength ranges between 5,000 to 6,000 psi. Elongation increases with the increase in NN concentration in the polymer, probably because of a decrease in crosslinking. Notch sensitivity increases with the increases in NN concentration. The softening point increases from 60°C to 96°C up to 30% NN concentration. Decrease in the softening point

above 30% NN may be explained if there is a phase separation in the polymer above that concentration or it may be due to incomplete conversion.

Mechanical properties were also evaluated by dynamic mechanical analysis. Figure 2 shows the effect of temperature on loss tangent for the polymers with different concentrations of NN. Tan delta max shifts toward higher temperatures with the increase in NN

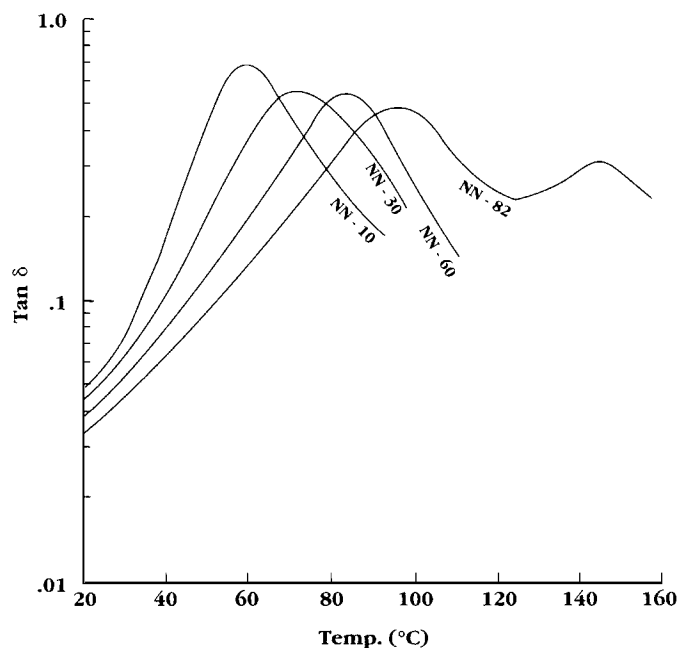


Figure 2 Tan δ vs. temperature for polydicyclopentadiene-co-polynorbornene nitrile (numbers after NN indicate % norbornene nitrile in the copolymer).

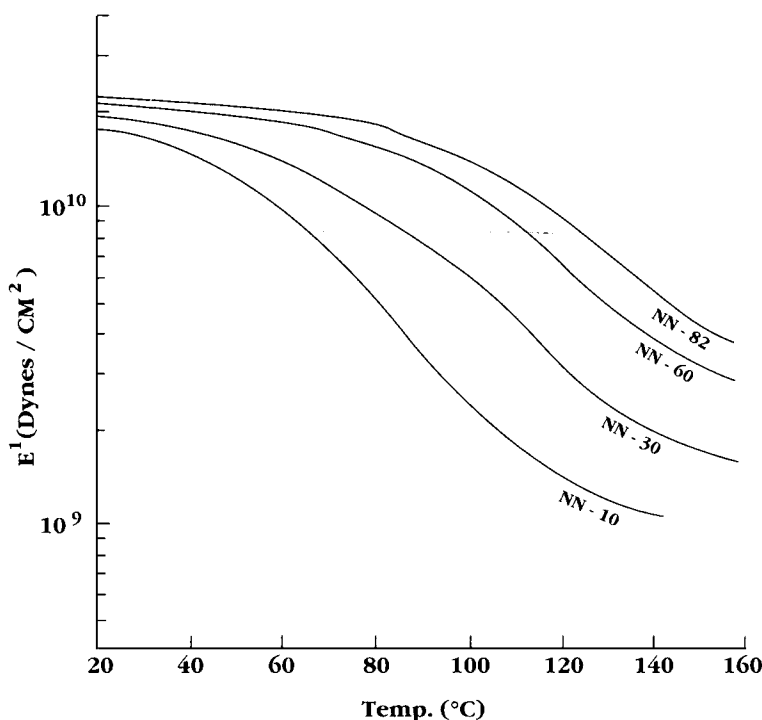


Figure 3 Dynamic modulus as a function of temperature for polydicyclopentadiene-co-poly-norbornene nitrile. (numbers after NN indicate % norbornene nitrile in the copolymer).

concentration. Only one tan delta max is observed up to 60% NN concentration, indicating that there is no phase separation between NN and DCPD and the polymer so prepared is a random copolymer. At concentrations above 60%, the copolymer PNN-82 shows two tan delta max—one at 142°C and the other at 90°C. Matsumoto reported the T_g of poly NN to be 140°C.¹⁰ The higher tan delta max (142°C) corresponds to the homopolymer of NN whereas the lower tan delta max (95°C) is in between the value of PNN and PDCPD. This indicates the presence of two phases, a pure PNN phase and a PDCPD phase, with a considerable amount of NN; the T_g for PDCPD is about 60°C.⁸

Figure 3 shows the effect of temperature on the dynamic modulus of PDCPD/PNN. The modulus increases with the increase in NN concentration. Although the increase in modulus at room temperature is only slight, the effect is more pronounced at higher temperatures. The retention of modulus at higher temperatures is much better for polymers with higher NN concentration. This is because of the increase in the value of tan delta max.

I would like to dedicate this work to the late Dr. Takayuki Murayama who helped enormously in our understanding of polymer science. His sudden death in November 1985 was a great loss to his colleagues.

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