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Metathesis copolymerization of 1,5-cyclooctadiene and norbornene with electrochemically generated WCl_6-based active species

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Abstract

The copolymerization of 1,5-cyclooctadiene and norbornene in the presence of an electrochemically generated WCl_6-based catalyst was investigated. This copolymer was isolated and characterized by ^1H, and ^{13}C NMR spectroscopy to analyse in detail the nature of homo- and heterodyad units and GPC analysis (Mn = 11200, PDI = 2.0). Homopolymerizations of 1,5-cyclooctadiene and norbornene were also studied and resulting polymers were characterized by spectroscopic methods to discuss with copolymers. Glass-transition temperatures of homo- and copolymers were determined by DSC.

Keywords: Metathesis copolymerization; 1,5-Cyclooctadiene; Norbornene; Reduction; WCl_6; NMR

1. Introduction

Cycloalkene copolymerizations have allowed elucidating aspects concerning the site of ring opening for different catalysts and classes of cycloalkenes. A wide variety of unsaturated copolymers can be synthesized using different catalyst systems [1]. Detailed ^{13}C NMR spectra of copolymers of cycloalkenes reveal the microstructures of these materials. Intensive studies have been carried out using cyclopentene and norbornene or 1,5-cyclooctadiene and norbornene mixtures [2–6].

This paper describes the investigation of the homo and copolymerizations of 1,5-cyclooctadiene (COD) and norbornene (NBE) in the presence of an electrochemically reduced tungsten based catalyst. The electrochemically reduction of WCl_6 and $MoCl_5$ produces metathetically active species [7,8]. A facile route for the electrochemically generation of an alkene metathesis catalyst from methylene chloride solution of WCl_6 was described by Düz et al. [9]. We previously reported the application of WCl_6-e-Al–CH_2Cl_2 catalyst system to cross-metathesis reactions of non-functionalized and functionalized acyclic alkenes [10–12] and ROMP of cyclododecene [13] and norbornene [14]. In the light of all of this, it was therefore useful to study the copolymerization reactions of 1,5-cyclooctadiene and norbornene with the same catalyst. The metathesis homopolymerizations of 1,5-cyclooctadiene and norbornene were also studied. We give a detailed ^{13}C NMR spectra of the ring opened copolymers of 1,5-cyclooctadiene and

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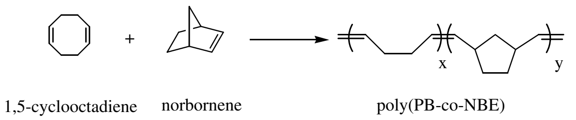
norbornene and derive information concerning dyad distribution and *cis–trans* double bond distribution.

2. Results and discussion

As yet there are relatively few quantitative studies of metathesis reaction of 1,5-cyclooctadiene and norbornene initiated by metathesis catalyst. Most catalyst systems used for ring opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene (COD) and norbornene (NBE) are W, Mo and Ru compounds [1–6,15–17]. We used a new technique to study the copolymerization reactions by ROMP. Metathesis reaction of 1,5-cyclooctadiene (M_1) with norbornene (M_2) in the presence of an electrochemically reduced tungsten based active species resulted in the formation of poly(PB-co-NBE) polymers as shown in reaction (1).



(1)

Table 1
Characterization of polymers synthesized by electrochemically produced W-based catalyst (catalyst/monomer$_{COD}$/monomer$_{NBE}$: 1:40:40)

Monomer	Properties of polymers	
1,5-Cyclooctadiene (COD)	σ_c	0.71
	PDI	1.7
	T_g (°C)	−11.39
	M_w	7600
	Yield (%)	38
Norbornene (NBE)	σ_c	0.55
	PDI	2.9
	T_g (°C)	29.93
	M_w	29700
	Yield (%)	72
1,5-Cyclooctadiene: norbornene (1:1)	σ_c	0.93 (M_1M_1), 0.55 (M_2M_2)
	PDI	2.0
	T_g (°C)	11.0
	M_w	11200
	Yield (%)	42

Homopolymerization reactions of 1,5-cyclooctadiene (COD) and norbornene (NBE) were also studied to compare with copolymerization reactions. A summary of the homo- and copolymerization results is shown in Table 1. The poly(PB-co-NBE) showed only one glass transition. The poly(PB-co-NBE) exhibits about 18.9 °C lower T_g and 22.4 °C higher T_g compared with homopolymers of NBE and COD, respectively. The DSC curves for polymers are given in Fig. 1. Gel permeation chromatographic analyses show only one peak for copolymer, confirming the formation and purity of copolymer. The 1,5-cyclooctadiene and norbornene polymerized with electrochemically reduced WCl_6-based

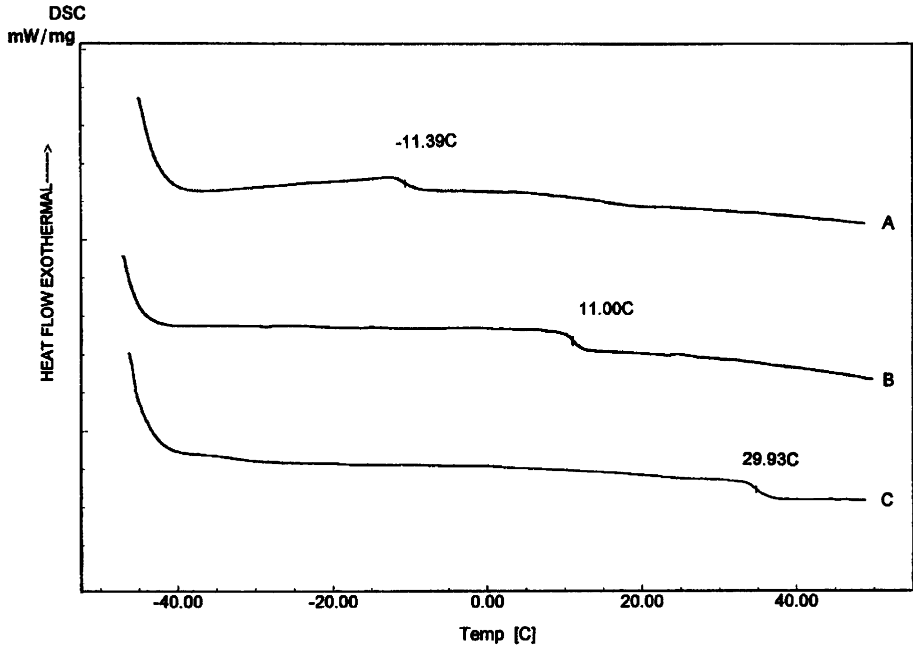


Fig. 1. The DSC curves for the polymers of (A) homo-COD, (B) co-COD-NBE and (C) homo-NBE.