

SHORT COMMUNICATIONS

Ring-Opening Polymerization of Methyl (*Z,E* or *E,Z*)-3,7-Cyclodecadienecarboxylate by Metathesis Catalysts

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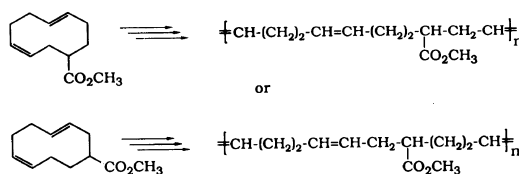
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It is generally known that in metathesis polymerization of cyclic olefins any substituents on the cyclic moiety usually exhibit unfavorable effect upon the polymerizability of the monomeric cyclic olefins and, in particular, most of metathesis catalysts are easily deactivated by polar substituents.^{1,2} For these reasons the substituted cyclic olefin systems have attracted rather less attention than those simpler cyclic olefins for the metathesis polymerization studies. However, the successful metathesis polymerization of certain cyclic olefins with properly positioned substituents can open new and interesting way to the preparation of olefin copolymers of controlled microstructures which are difficult to obtain by

other means.^{3,4}

In the present paper we would like to report the polymerization of methyl (*Z,E* or *E,Z*)-3,7-cyclodecadienecarboxylate (MCDC). It was expected that the polymer had the structure in that methyl acrylate and butadiene were incorporated in 1 to 2 ratio in alternating fashion *via* ring-opening polymerization (Scheme 1).



Scheme 1.

Table I. Polymerization of MCDC with various catalyst systems^a

Run ^b No.	Catalyst × 10 ⁻⁴ mol	Cocatalyst × 10 ⁻⁴ mol	Conversion	η_{inh}^c
			%	dl g ⁻¹
1	X = Me (2)	PbEt ₄ (4)	17	0.08
2	X = Cl (2)	PbEt ₄ (4)	25	0.12
3	X = Ph (2)	PbEt ₄ (4)	56	0.23
4 ^d	WCl ₆ (4,8)	SnMe ₄ (20,40)	—	—

^a Monomer, 1.87 ml (1.94 g); reaction time, 4 h; temperature, 60°C.

^b In Run No. 1—3, the catalyst was WCl₄ (OAr)₂ [OAr = O-2,6-C₆H₃X₂].

^c 0.5 g dl⁻¹ in toluene at 25°C.

^d Polymerization was carried out at 80°C.

Polymerization was carried out with two kinds of catalyst systems, WCl₆/SnMe₄ and WCl₄ (O-2,6-C₆H₃X₂)₂ (X = Ph, Me, Cl)/PbEt₄. These catalyst systems are well known having a good tolerating property to ester functional group in metathesis reactions.^{5,6} MCDC was prepared by the method of C. Dellichhausen from methyl acrylate and butadiene with Ni(Acac)₂-AlEt₂(OEt)-(O-2-C₆H₄C₆H₅)₃P as a catalyst system.⁷ And the catalyst WCl₄ (O-2,6-C₆H₃X₂)₂ (X = Ph, Me, Cl) were prepared by the reaction of WCl₆ with the appropriate phenol according to procedures already described by Quignard *et al.*⁸

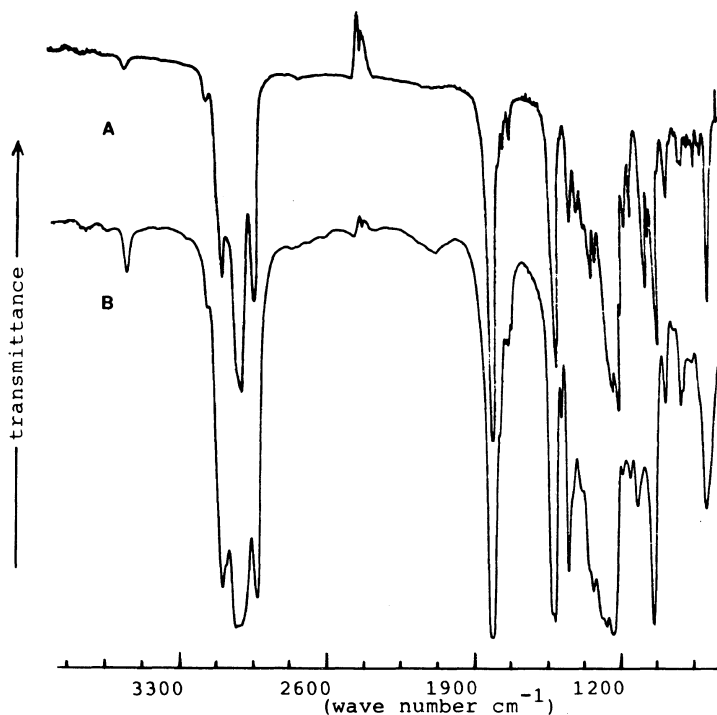
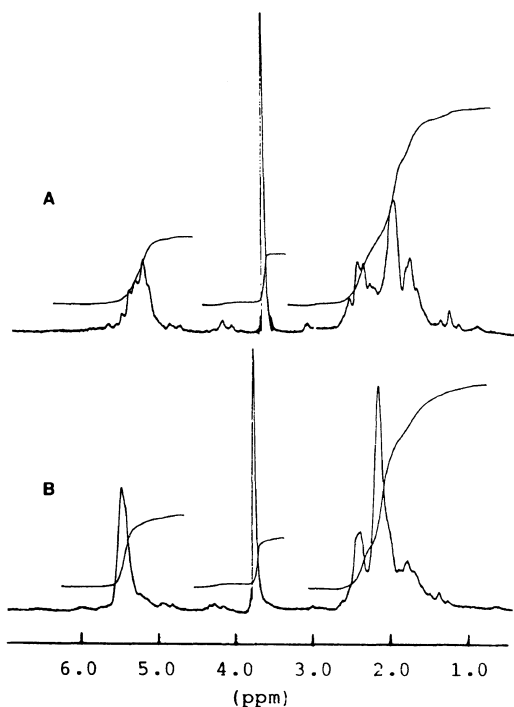


Figure 1. IR spectrum of monomer (A) and polymer (B) catalyzed by $WCl_4(O-2,6-C_6H_3(Ph)_2)_2/PbEt_4$ (Run No. 3).



In the homogeneous metathesis reactions of cyclic olefins containing ester functional group, $WCl_6/SnMe_4$ is so far the best known catalyst system. Unfortunately $WCl_6/SnMe_4$ did not show any activity for the polymerization of MCDC. However, ring-opening metathesis polymerization of MCDC could be achieved with the catalyst systems composed with the $WCl_4(O-2,6-C_6H_3X_2)_2$ ($X = Ph, Me, Cl$) and $PbEt_4$. The polymerization results are summarized in Table I.

For the given cocatalyst $PbEt_4$ and the given time period of polymerization reaction, the conversion of the polymerization varied depending on the nature of the substituents at 2,6-position of the phenyl group ($X = Me < Cl < Ph$) of main catalyst. The polymers obtained

Figure 2. 1H NMR spectrum of monomer (A) and polymer (B) catalyzed by $WCl_4(O-2,6-C_6H_3(Ph)_2)_2/PbEt_4$ (Run No. 3).

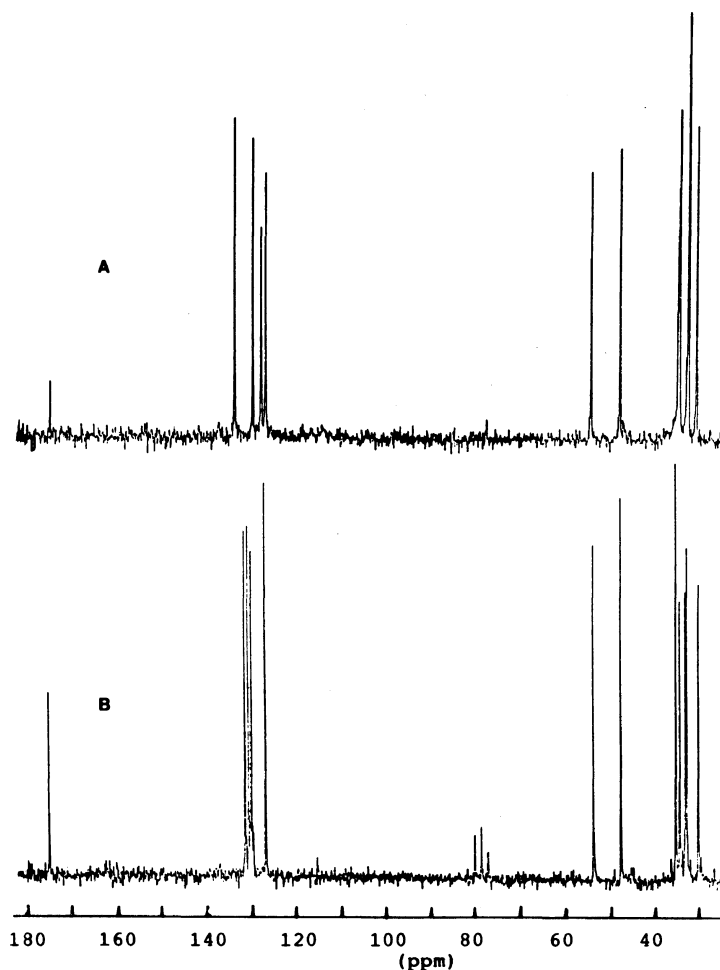


Figure 3. ^{13}C NMR spectrum of monomer (A) and polymer (B) catalyzed by WCl_4 (O-2,6- $\text{C}_6\text{H}_3(\text{Ph})_2$) $_2/\text{PbEt}_4$ (Run No. 3). Chemical shift are referenced to CDCl_3 (77.0 ppm).

were soluble in ordinary organic solvents such as chloroform, dichloromethane and benzene. The structures of the polymers were confirmed by infrared, ^1H NMR and ^{13}C NMR spectra. In infrared spectra the absorption band near 1734.4 cm^{-1} is attributable to ester carbonyl. The absorption at 987.0 cm^{-1} and at 917.4 cm^{-1} are corresponding to *cis* and *trans* double bonds (Figure 1). The ^1H NMR spectra of the polymers show olefinic (5.2—5.6 ppm): methoxy (3.6—3.8 ppm): other protons (1.2—2.7 ppm) in the correct ring-opened proportion of 4:3:11. (Figure 2).

The assumed structure of the polymer was further confirmed by ^{13}C NMR spectra. Olefinic carbons of the polymer appeared at 127.8—132.6 ppm in multiplet being different from those of MCDC. MCDC showed distinctive four peaks in relatively broad range 128.1—135.1 ppm (Figure 3).

A remarkable fact is that the polymer, within the limits of analytical error, is free of the vinylic addition products which are the typical side reaction products in metathesis polymerization catalyzed by tungsten hexachloride-organaluminum. It resulted from the

low acidity of $\text{WCl}_4(\text{OAr})_2/\text{PbEt}_4$.⁹

In conclusion, the cyclodecadiene containing ester functional group (MCDC) undergoes ring-opening metathesis polymerization by the catalyst system $\text{WCl}_4(\text{OAr})_2/\text{PbEt}_4$ to afford a 1:2 copolymer of methyl acrylate and butadiene. It is also interesting to note that ring-opening metathesis polymerization of other substituted cyclodecadienes obtained from MCDC by functional group transformation will be expected to give various butadiene-based copolymers. Further work on similar monomer systems as well as other catalyst systems is now in progress and a full account of the work will be published elsewhere.

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