

SHORT COMMUNICATIONS

Ring-Opening Metathesis Polymerization of 4,6-Diphenylcyclooctene: 2:1 Alternating Copolymer of Styrene and Butadiene

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In the copolymer systems composed of different kind of monomers, the mer sequences of the polymers can exhibit significant effect on the physical properties of polymers.¹ Ring-opening metathesis polymerization (ROMP) is unique method to obtain double bond-containing alternating copolymers.² Particularly, ROMP of 4,6-disubstituted cyclooctenes could provide the alternating copolymers of one butadiene and two vinylics. However, any substitution on cycloolefins gives an adverse effect on their polymerizability and the syntheses of 4,6-disubstituted cyclooctenes are formidable tasks. For these reasons, the 4,6-disubstituted cyclooctenes have attracted rather less attention for ROMP studies.

In the present paper, we report the synthesis

of new monomer, 4,6-diphenylcyclooctene (DPCO) and its polymerization to poly(4,6-diphenyl cyclooctenylyene) which has the structure in that styrene and butadiene are incorporated in 2 to 1 ratio in alternating fashion.

The DPCO was prepared by reduction of 2,8-diphenyl-4-cycloocten-1-one which was prepared by α '-arylation of 2-phenyl-5-cycloocten-1-one(PCON) with diphenyliodonium chloride and LDA.³ The PCON was prepared according to the reported method.⁴

Polymerizations were carried out with various metathesis catalyst systems.⁶ The results of polymerizations are summarized in Table I. The catalyst system of $WCl_4(OAr)_2/Pb(Et)_4$ ⁵ gave high molecular weight polymers

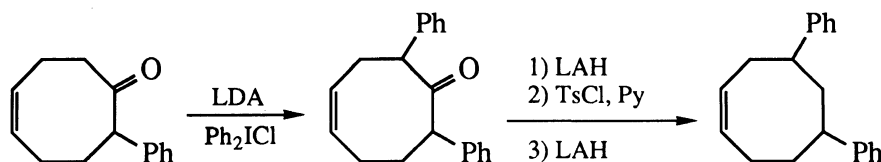
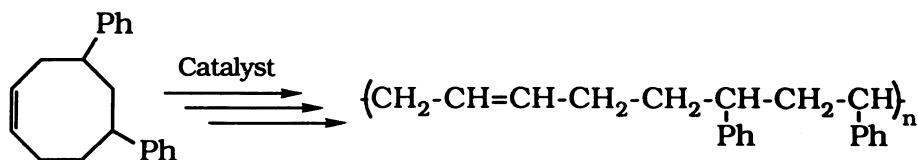


Table I. Polymerization of DPCO with various catalyst systems

Catalyst system		Monomer/Cat.	Temp	Time	Yield	η_{inh}^b
mole ratio		mole ratio	°C	h	%	dl g ⁻¹
WCl ₆ -Et ₂ AlCl	(1:4)	50:1	25	48	Trace	—
WCl ₄ (OAr) ₂ -Et ₂ AlCl	(1:2)	50:1	25	48	Trace	—
WCl ₄ (OAr) ₂ -Pb(Et) ₄	(1:2)	50:1	15	24	84	0.33
WCl ₄ (OAr) ₂ -Pb(Et) ₄	(1:2)	100:1	15	24	87	0.62
WCl ₄ (OAr) ₂ -Sn(Bu) ₄	(1:2)	50:1	15	24	62	0.23

^a -OAr was 2,6-diphenylphenoxy group.

^b 0.5 gd^l⁻¹ in toluene at 15°C.

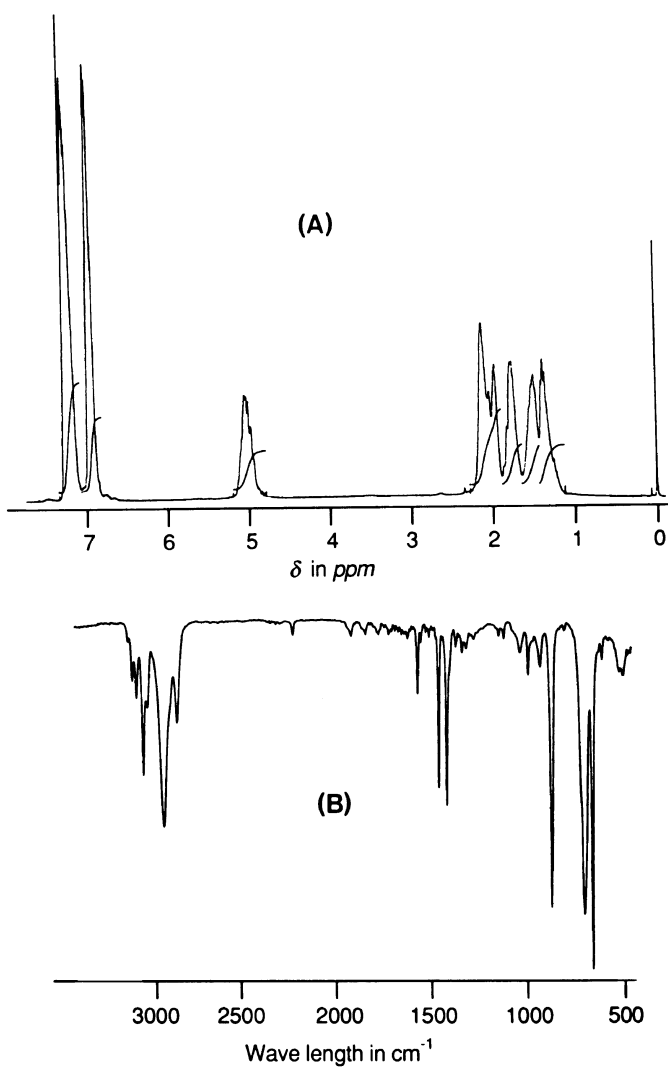


Figure 1. ¹H NMR (A) and IR (B) spectra of the polymer obtained with catalyst system of WCl₄(OAr)₂/Pb(Et)₄.

in high conversion.

The polymers obtained were soluble in ordinary organic solvents such as chloroform, tetrahydrofuran (THF) and toluene, and possessed the presumed structure as indicated by their ^1H NMR and IR spectra (figure). The ^1H -NMR spectrum of the polymers show phenyl protons (7.6–7.1 ppm), vinyl protons (5.3–4.7 ppm), and other aliphatic protons (2.7–1.3 ppm) in the correct proportion of ring opened mers of 10:2:10. The IR spectrum of the polymers exhibited absorption band at 911 cm^{-1} and 742 cm^{-1} attributable to $=\text{C}-\text{H}$ out-of-plane bending of *trans* and *cis* double bond, respectively.

In conclusion, the DPCO is prepared *via* α' -arylation and reduction of the PCON. ROMP of the DPCO by the catalyst system of $\text{WCl}_4(\text{OAr})_2/\text{Pb}(\text{Et})_4$ afford 1:2 alternating copolymers of butadiene and styrene. It is also interesting to note that these copolymers have homogeneous composition along the whole chain whereas there are some block segments in the conventional copolymers of styrene and butadiene. The obtained polymer are plastic materials, exhibiting glass transition around 36.4°C . This is in accordance with the value expected from the equation of Wood for the copolymers of butadiene and styrene prepared at 5°C .⁷

Further work on ROMP of other 4,6-disubstituted cyclooctenes is now in progress and a full account of the work will be published elsewhere.

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REFERENCES AND NOTES

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3. 51.4 ml of *n*-butyllithium (0.13 mol, 2.5 M in hexane) was added dropwise to diisopropylamine (13.0 g, 0.13 mol) in 50 ml of anhydrous THF at -78°C . After the addition was completed, the reaction mixture was allowed to come to room temperature and stirred there for 30 min. The solution was recooled to -78°C , followed by the dropwise addition of 50 ml anhydrous THF solution of PCON (25 g, 0.13 mol) and stirred for 2 h. The resulting enolate solution was added dropwise with cannular to 500 ml ammonia solution of diphenyliodonium chloride (44.3 g, 0.14 mol). After standing for 4 h, ammonia was allowed to evaporate and the resulting solution was extracted with ether. The solid obtained by evaporation of the solvent was recrystallized from ether-hexane as white crystal: 15.2 g, 55 mmol (yield 44.1%); mp 147°C ; 300 MHz ^1H NMR (CDCl_3) $\delta=7.30-7.23$ (m, 5H), $\delta=7.05-7.01$ (m, 3H), $\delta=6.66-6.63$ (m, 2H), $\delta=5.89-5.83$ (m, 2H), $\delta=3.95-3.90$ (dd, 1H), $\delta=3.88-3.82$ (dd, 1H), $\delta=3.38-3.26$ (m, 1H), $\delta=2.52-2.41$ (m, 2H), $\delta=2.28-2.21$ (m, 1H), $\delta=2.07-1.94$ (m, 1H), $\delta=1.76-1.68$ (m, 1H). ^{13}C NMR: $\delta=211.1$, 141.2, 135.4, 131.4, 129.2, 128.6, 128.0, 127.8, 127.7, 127.6, 126.3, 61.9, 52.6, 33.6, 26.5, 25.5.
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6. Polymerization procedure by the catalyst systems was proceeded as follows; The weighed $\text{WCl}_4(\text{OAr})_2$ was dissolved in toluene to be 0.05 N solution. The corresponding amount of cocatalyst was added at 80°C and the resulting solution was aged for 5 min at that temperature. Then the catalyst solution was added to the degassed monomer.
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