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Ring–Opening Polymerizations for the Synthesis of Sequence–Controlled Copolymers

Iwhan Cho

Department of Chemistry, Korea Advanced Institute of Science and Technology, 373-1 Gusung-dong, Yusung-gu, Daejeon, Korea
E-mail: cho@kaist.ac.kr

Summary: Various prestructured cyclic monomers were synthesized and polymerized to construct the copolymers of controlled mer sequence. Substituted 8-, 10- and 12-membered cyclic olefins were polymerized by ROMP catalyst, i.e., $W(OAr)_2Cl_4/Et_4Pb$. Those polymers obtained were the alternating terpolymers of butadiene and vinyl monomers. Cyclic monomers with mesogenic groups as substituents were prepared and polymerized successfully. The resulting polymers were highly liquid crystalline exhibiting rather lower transition temperatures than their monomeric analogs.

Keywords: ring-opening polymerization; ROMP

In the copolymer systems, the mer sequence could exhibit significant effect on the physical properties of polymers. Thus, many research groups have searched for new monomer-to-polymer systems in that the microstructure of the copolymers can be controlled. Ring-opening polymerization of prestructured cyclic monomers has been an attractive method for this purpose. The cyclic monomers in which the monomers to be used in copolymerization are properly incorporated in certain stoichiometry would lead upon polymerization to the copolymers of controlled mer sequence. Recently, we have carried out the ring-opening polymerization of substituted 8-, 10- and 12-membered cyclic olefins which were prepared from readily available starting materials and the multi-component copolymers of the controlled mer-sequence were obtained. Our work on this subject has been reviewed recently.[1]

1. Ring-Opening Metathesis Polymerization of Disubstituted Cyclooctenes

Among the butadiene-based copolymers the styrene-butadiene elastomers (SBR) are particularly notable because of their wide commercial exploitations. However, the control of microstructure is still the subject of many studies and the way to control mer sequence is yet to be found (except block copolymers). The control of mer sequence of the copolymer is expected to exhibit profound effect on their properties such as wear/traction properties, abrasion resistance etc., when the polymer is applied to their formulations.

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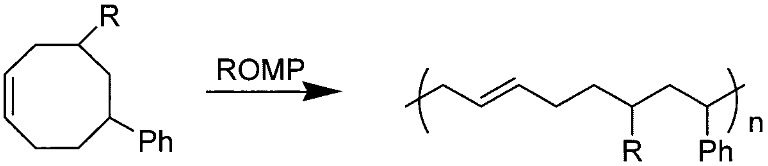
We have worked on various cyclic monomers which would lead to the sequence-controlled styrene-butadiene copolymers upon ring-opening polymerizations[2]: 1-Vinyl-4-phenylcyclobutane[3], 2-phenyl-4-vinylsulfone[4]. Our work is now turned to 8-, 10- and 12-membered cyclic olefin systems (**1a, 1b** and **1c**) in that these cyclic olefins with proper substituents were synthesized and polymerized with metathesis catalysts to obtain various sequence-controlled co- and ter-polymers.



1a R=H ethylene, styrene and butadiene terpolymer

1b R=CH_3 propylene, styrene and butadiene terpolymer

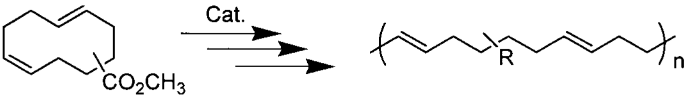
1c R=Ph styrene and butadiene 2:1 copolymer

The synthesis of these monomers was rather elaborate and tedious. The exact procedures have been reported elsewhere.[5] These cyclooctene derivatives exhibited quite different polymerization behavior depending upon the catalyst systems employed. The catalyst system of $W(OAr)_2Cl_4/Et_4Pb$ was found to be most effective. The polymers of 4-methyl-6-phenylcyclooctene (**1a**) were rubbery exhibiting the glass transition at -3.6 °C. They were soluble in THF, toluene and methylene chloride. The analysis of the IR, ^{1}H-NMR, and ^{13}C-NMR confirmed the structure of 1:1:1 alternating terpolymer of ethylene, propylene and styrene.

The polymer of 4,6-diphenylcyclooctene (**1c**) was glassy and soluble in THF, toluene and methylene chloride. The glass transition measured by DSC was 39.2°C. The structure of the polymer was confirmed to be a 2:1 alternating copolymer.

2. Polymerization of Cyclodecadiene Derivatives

Various substituted cyclodecadienes, methyl(Z,E or E,Z)-3,7-cyclodecadienyl carboxylate (**2a**), (Z,E or E,Z)-3,7-cyclodecadien-1-carboxylic acid (**2c**), (Z,E or E,Z)-3,7-cyclodecadienylmethanol (**2d**), and 8- or 9-methyl(Z,E)-1,5-cyclodecadiene (**2b**) were prepared and their polymerization were carried out with several catalyst systems.[6]

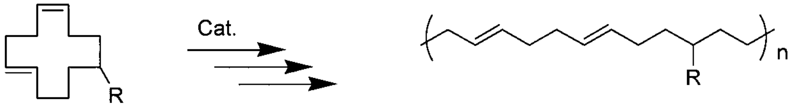


2a R=CO_2CH_3 **2c** R=CO_2H
2b R=CH_3 **2d** R=CH_2OH

Those four cyclodecadiene derivatives exhibited quite different polymerization behaviors depending upon the catalyst systems employed, reaction temperature and reaction time. **2a** underwent ring-opening metathesis polymerization by $WCl_4(O\text{-}2,6\text{-}C_6H_3X_2)_2$ (X=Ph, Me, Cl)/$PbEt_4$. IR and NMR spectra of monomers and polymers confirmed that the resulting polymers had structure in that methyl acrylate and butadiene were incorporated by 1 to 2 ratio in alternating fashion. In the polymerization of (Z,E or E,Z)-3,7-cyclodecadien-1-carboxylic acid (**2a**), the successful ring-opening polymerization could be achieved with WCl_6/Et_3Al and $MoCl_5/Et_3Al$. The resulting polymer was powdery and insoluble in common organic solvents such as chloroform, benzene and acetone, but soluble in trifluoroacetic acid. (Z,E or E,Z)-3,7-Cyclodecadienylmethanol(**2d**) was also prepared and subjected to polymerization. When the polymerization of 8- or 9-methyl(Z,E)-1,5-cyclodecadiene(**2b**) was carried out with $WCl_6/EtAlCl_2$ and $WCl_4(O\text{-}2,6\text{-}C_6H_3Ph_2)_2$ /$PbEt_4$, small extent of addition product was incorporated into the resulting polymers obtained in the case of $WCl_6/EtAlCl_2$. However, the polymer obtained with $WCl_4(O\text{-}2,6\text{-}C_6H_3Ph_2)_2$ /$PbEt_4$ was free of vinylic addition product.

3. Polymerization of Cyclododecadiene Derivatives

In the synthesis of the butadiene-based sequence-controlled copolymers, the following cyclododecacene monomers were successfully prepared and polymerized : 9-Phenyl-1,5-cyclododecadiene(**3a**)^7, 9-methyl-1,5-cyclododecadiene(**3b**), 9-acetyl-1,5-cyclododecadiene(**3c**), methyl-4,8-cyclododeca-dienecarboxylate(**3d**) and 1,5-cyclododecadiene(**3e**).



3a R=Ph **3c** R=$OCOCH_3$ **3e** R=H
3b R=CH_3 **3d** R=CO_2CH_3

The monomer **3a** was polymerized with various metathesis polymerization catalyst systems including W. The polymer was rubbery at room temperature and the glass transition was observed at –33.6 °C. The analysis of the ^{1}H-NMR and ^{13}C-NMR spectra confirmed the structure of 2:1:1 alternating copolymer of butadiene, ethylene and propylene. The polymer of **3c** and the polymer of **3d** were the 2:1:1 copolymer of butadiene, ethylene and vinylacetate, and the 2:1:1 copolymer of butadiene, ethylene and methylacrylate. And the polymer of **3e** gave 2:2 alternating copolymer of butadiene and ethylene. For the purpose of comparision with commercial SBR the copolymerization of **3a** with 1,5,9-cyclododecatriene, a trimer of butadiene was carried out with monomer mixtures of different feed ratios. The copolymerization of 7:10 mixture of 3a and 1,5,9-cyclododecatriene by $WCl_4(OAr)_2/PbEt_4$ in chlorobenzene at 80°C gave high molecular weight (η_{inh} = 1.45 dl/g) polymer in good conversion (87%). The ^{1}H NMR spectrum of the copolymer was analyzed to determine the copolymer composition confirming that the copolymer composition was close to monomer feed ratio. The copolymer obtained from monomer feed ratio 7 to 10 contained 24% (by weight) of styrene, about the same level of styrene content of commercial SBR. Commercial SBRs were known to have the structural irregularities containing 1,2-polymerized butadiene and grafted side chains. However, the copolymer obtained here ROMP of **3a** and cyclic butadiene trimer was supposed to be linear with T_g at -61 °C which was comparable to that of commercial SBR (T_g = -59 ~-64°C). Efforts were made to detect any phenomena related with stretch crystallization with this material but failed. The other aspect of material properties was left to be investigated.

4. Applications to Liquid Crystalline Polymers

It was enunciated that a flexible spacer should be inserted between the polymeric main chain and the mesogen pendent groups to decouple the motions of side groups from that of main chain in the liquid crystalline states.[8] Various esters were employed to be used as spacers but the side chain liquid crystal polymers with a methylene chain spacer (no polar functional group) in the backbone was not prepared. Since the synthesis of new cyclic monomer systems and their polymerizations to obtain hydrocarbon copolymers of strict mer sequences and application of this method to the synthesis of a side chain liquid crystal polymer was rather unique.

A side chain liquid crystal polymer with flexible spacer backbone (12-methylene repeating unit with a mesogen side chain) and no spacer in the side chain was prepared. 4,8-Cyclododecadienyl 4'-methoxy-4-biphenyl terephthalate (**4a**) was prepared by the reaction of

4,8-cyclodecadienol with terephthaloyl chloride followed by the reaction with methoxy biphenol.

The monomer **4a** was polymerized with $WCl_4(OAr)_2/PbEt_4$ at 80°C in toluene and the polymer was obtained in 95% conversion and the molecular weight was 15,400 (M_w/M_n = 2.3). This polymer with backbone unsaturation was hydrogenated over Pd/C catalyst at room temperature in THF. The resonance peaks in ^1H NMR and the absorption in IR spectrum due to the backbone unsaturation disappeared completely in the spectra of the final polymer: 5:1 Copolymer of ethylene and vinyl mesogenic ester. The both saturated and the unsaturated polymers were soluble in common solvents such as $CHCl_3$ and THF. When solution-cast, the polymer gave turbid white films.[9]

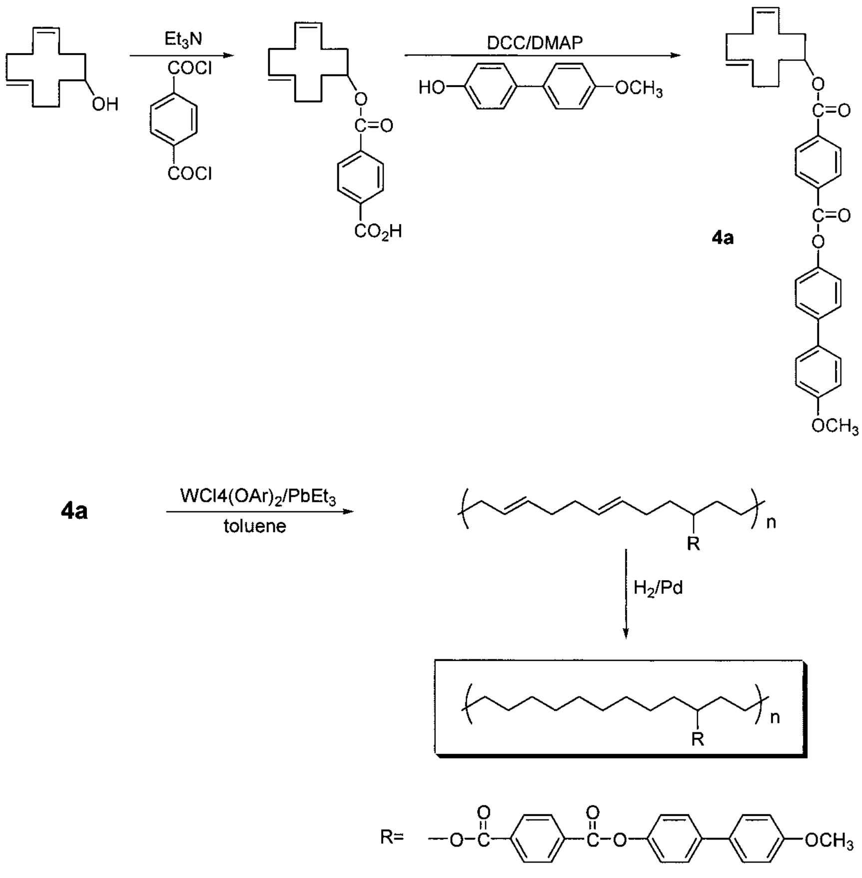
The phase transition temperatures of the monomer **4a** and its unsaturated and saturated polymers are summarized in Table **1**. It was usual observation that the polymers showed their phases at higher temperatures than their monomeric analogues. However, in the present case the polymers exhibited their transitions at much lower temperatures than the monomer. And the transition temperature of the saturated polymer was lower than that of unsaturated polymer. It was conceived to be due to easier rotation of the main chain bondings.

Table 1. Phase transition temperature of **4a** and its polymers (from second heating/cooling cycle) (Key: K, crystalline; G, glassy; S, smectic; N, nematic; I, isotropic. Heating/cooling rate = 10°C/min)

	Phase transition temperature (°C)
4a	$K \underset{75}{\overset{83}{\rightleftharpoons}} S \underset{114}{\overset{149}{\rightleftharpoons}} N \underset{114}{\overset{149}{\rightleftharpoons}} I$
4a Polymers unsaturated	$G \underset{57}{\overset{62}{\rightleftharpoons}} S \underset{110}{\overset{116}{\rightleftharpoons}} N$
4a Polymers hydrogenated	$G \underset{56}{\overset{61}{\rightleftharpoons}} S \underset{100}{\overset{113}{\rightleftharpoons}} N$

Thin film X-ray diffraction experiment indicated that the monomer **4a** exhibited nematic and smectic texture while the polymers exhibited only smectic textures.

In another system investigated, cholesterol was introduced as a mesogen instead of methoxy biphenol. Again in the final polymer failed to exhibit cholesteric phase, while the monomer was a cholesteric liquid crystal. The polymeric cholesterol-containing system in which cholesteryl groups could pack helically exhibiting cholesteric liquid crystal phase remained to be synthesized.



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