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Olefin Metathesis of Cyclohexene

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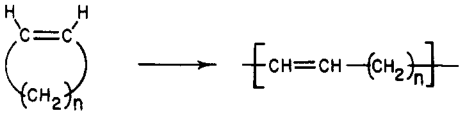
While strained cyclic olefins readily undergo metathesis polymerization[1] (eq 1), cyclohexene is reportedly inert to



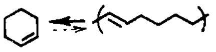
(1)

metathesis conditions owing to the thermodynamic stability of its six-membered ring.[2] The position of equilibrium between monomer and ring-opened products can be expressed as the ratio of propagation and depropagation rate constants and is a function of temperature, concentration, and changes in the enthalpy and entropy for the process (eq 2 and 3).

$$K_{\mathrm{eq}} = k_{\mathrm{propagation}}/k_{\mathrm{depropagation}} \qquad (2)$$

$$\Delta G = -RT \ln K_{\mathrm{eq}} = \Delta H - T\Delta S \qquad (3)$$

Entropy changes for ring-opening polymerization are generally negative, due primarily to the loss in translational entropy of the monomer. High monomer concentration attenuates this effect, but does not completely eliminate the positive contribution to the free energy of polymerization. If polymerization is to occur, this positive contribution must be offset by a sufficiently negative enthalpy change. For ring-opening polymerizations, the same bonds are present in monomer and polymer, thus ΔH is a function primarily of strain energy in the monomer. Having a strain energy greater than a certain minimum value is therefore a basic criterion for ring-opening polymerization of any cyclic monomer.[3] Comparing the monomer/polymer equilibrium positions for cyclobutene and cyclohexene metathesis under conditions generally employed for these reactions illustrates the effects of ring strain (eq 4 and 5).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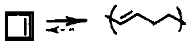
(5)

Cyclobutene (31 kcal/mol strain energy) is converted quantitatively to polymer,[4] while cyclohexene (2.5 kcal/mol strain energy) forms no ring-opened products.[2] The reverse of eq 4, the conversion of polyenes containing 1,7-diene units to cyclohexene, has been reported several times.[5]

The objective of the research reported here was to overcome cyclohexene's resistance to metathesis. Two approaches were followed: One involves lowering the temperature and increasing the cyclohexene concentration. If ΔH is only slightly negative, it follows from eq 3 that at low-enough temperatures, cyclohexene will polymerize. ΔH for conversion of liquid cyclohexene to solid amorphous linear polymer has been estimated to be 2 and −2 kJ/mol for the cis and trans polymer, respectively.[6] Many monomers exhibit ceiling temperatures, the temperature above which, for a given monomer concentration, no polymer can form.[7] The other approach takes advantage of kinetics. If the propagation rate can be increased relative to the depropagation rate (eq 2) for a period of time and the reaction stopped before equilibrium is reached, polymer can be "trapped". This can be accomplished by the addition of a second monomer. Recently we reported[8] that the addition of norbornene significantly increases the rates of cyclooctene and cyclooctadiene propagation.

A third strategy toward the metathesis of cyclohexene has been reported and has met with moderate success: under high pressures the loss in entropy upon metathesis addition is less detrimental to the equilibrium. At 10 000 psig cross metathesis between cyclohexene and ethylene yields 6.8% 1,7-octadiene.[9]

Experimental Section

General. All manipulations were carried out under an atmosphere of prepurified nitrogen. Toluene (Fisher), cyclohexene (Eastman), and tetramethyltin (Aldrich) were refluxed over calcium hydride and distilled under nitrogen. Norbornene (Aldrich) (2.25 M in toluene) was stirred for 12 h over calcium hydride, degassed, and distilled trap-to-trap. Tungsten hexachloride was zone refined under vacuum at 350–400 °C and stored under nitrogen. Ozone was generated with a Welsbach T-408 ozone generator. Gas chromatographic analyses were performed on a Hewlett-Packard 5790A gas chromatograph and an OV-101 column (5% on Chromosorb P 5.5 ft × 0.125 in.).

Cyclohexene Homometathesis. Cyclohexene (5.0 mL, 49 mmol) is dissolved in 5 mL of toluene in a Schlenk flask. Tetramethyltin (0.15 mL (0.36 mmol) of 2.4 M in toluene) is added followed by 1.5 mL of 0.1 M tungsten hexachloride in toluene (0.15 mmol). After 10–15 min at 25 °C the reaction is cooled to the temperature of the study. The disappearance of cyclohexene is followed by gas chromatography. Toluene serves as the internal standard.

To isolate metathesis products, wet acetone is introduced at low temperature. The insoluble catalyst residue, and any precipitated product, is removed by filtration, dried, and washed with toluene to recover reaction products. This toluene solution is combined with original filtrate. Solvent and monomer are removed under vacuum (30 mm) to leave an oily residue. This is transferred, under nitrogen, to a short path length still and distilled under vacuum; the last fraction distilling at 3 mm and 130 °C: IR consistent with predominantly cis alkene; ^{1}H NMR δ 1–2 (br, m), 5.3 (m).

Metathesis Decomposition of Cyclohexene Oligomers. The oligomer mixture (1.5 mL) is diluted with toluene (~4.5 mL) to yield a solution ~20% w/v in oligomer. This solution is dried over CaH_2 and distilled under a reduced pressure of nitrogen (3 mm, 100 °C). To this is added 0.072 mmol of tetramethyltin (0.03 mL of a 2.4 M chlorobenzene solution of tetramethyltin) and 0.3 mL of a 0.1 M chlorobenzene solution of tungsten hexachloride (0.03 mmol tungsten) and 0.5 mL of cyclohexene as an internal standard. The decrease in oligomer concentration, and increase in cyclohexene concentration, is monitored by GC, using both chlorobenzene and toluene as internal standards.

Cyclohexene–norbornene copolymerizations are carried out in a manner similar to cyclohexene homometathesis. The procedure above is repeated, and the equilibrium cyclohexene concentration is determined by GC. Norbornene (1 mL (2.25 mmol) of 2.25 M in toluene) is introduced, and changes in cyclohexene and norbornene concentrations are monitored by GC. The catalyst is deactivated with wet acetone as soon as norbornene is no longer detected.

Copolymer Composition Determination by Ozone Degradation. The copolymer is precipitated from the reaction solution with methanol, filtered, and dried under vacuum. Polymer (1.7 g) is dissolved in 40 mL of dichloromethane, and the ozonolysis and subsequent degradation of the ozonide (Zn/acetic acid) are carried out according to literature procedures.[10] Reduction of the resulting dialdehydes with lithium aluminum hydride[11] and fractional vacuum distillation (0.5 mm) render 1,6-hexanediol (92 °C) and 1,3-bis(hydroxymethyl)cyclopentane (118 °C). IR and ^{1}H NMR spectroscopy and GC retention times against standards of the two diols confirm their identities. GC analysis of the crude reaction products yields an accurate estimate of the relative amounts of each monomer in the copolymer (GC response factors were determined from standards).

Results and Discussion

Cyclohexene Homometathesis. When 5 M cyclohexene in toluene is treated with tungsten hexa-

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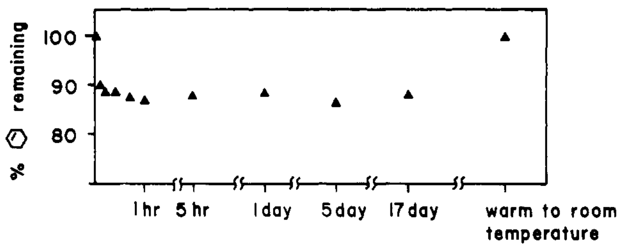

Figure 1. Metathesis of cyclohexene at −77 °C. Initial tungsten:tin:cyclohexene ratio 1:1:6.3.

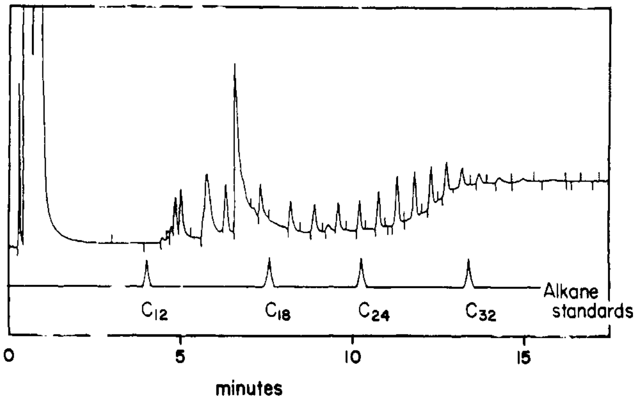

Figure 2. Gas chromatogram of cyclohexene metathesis products of reaction at −77 °C. Elution times of alkane standards are indicated. 100 °C for 2 min, 100–300 °C at 22 °C/min, 300 °C for 5 min.

chloride/tetramethyltin at room temperature, no change in cyclohexene concentration occurs, as evidenced by gas chromatography. Lowering the temperature to −77 °C causes a decrease in cyclohexene concentration to 88% of its original 5 M (Figure 1). This composition is stable for days at this temperature; the equilibrium shifts back to 100% monomer upon warming to room temperature. Destroying the catalyst by adding cold wet acetone to the reaction mixture at −77 °C permits the isolation of metathesis products. Gel permeation chromatography indicates only that the products are oligomers with molecular weights below the limits of a 500-Å column. Gas chromatography indicates a mixture of oligomers in the 2–6 DP range (Figure 2). This is the upper limit of the analytical technique; slightly higher MW oligomers may be present as well. The larger number of peaks in the gas chromatogram indicates that different geometric isomers of the various oligomers are formed. The mixture exhibits infrared and ^{1}H NMR spectra consistent with predominately *cis*-cyclohexene oligomers, but the most convincing structural evidence is that an isolated mixture of oligomers is converted back to cyclohexene upon exposure to metathesis catalysts.

Equilibrium concentrations of cyclohexene were determined at four temperatures: −45, −63, −77, and −84 °C. The logarithm of the equilibrium cyclohexene concentration was found to vary linearly with T^{-1} (Figure 3). Extrapolation to 100% cyclohexene (5 M) indicates that productive metathesis occurs below about −23 °C. Ceiling conditions were clearly not achieved; no high polymer was obtained. The most severe conditions attempted were 7.5 M cyclohexene and −116 °C.

Cyclohexene–Norbornene Copolymerization. As discussed above, cyclohexene is inert to metathesis catalysts at 25 °C. When norbornene (0.23 equiv, based on cyclohexene) is added to a mixture of active metathesis catalyst in 0.1 M cyclohexene, however, cyclohexene is consumed. Figure 4 describes this experiment. During the 1 min that norbornene is present (it polymerizes rapidly under these conditions), 5% of the cyclohexene is consumed. This corresponds to a norbornene copolymer containing 18% cyclohexene. That this is a kinetic product is evidenced by the fact that cyclohexene concentration returns to 99% of its original value when the copolymer/cyclohexene catalyst mixture is stirred at room temperature overnight. Deactivation of the catalyst with wet acetone immediately after the completion of norbornene polymerization permits the isolation of copolymer. Ozone degradation of a copolymer sample isolated by precipitation from methanol followed by lithium aluminum hydride reduction renders the two expected diols, with 1,6-hexanediol comprising 7.5% of the product.

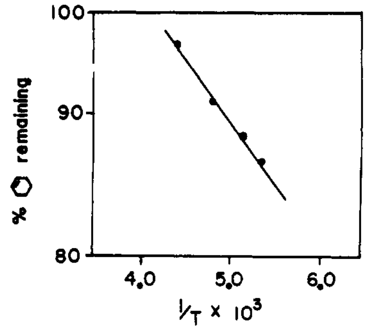

Figure 3. Temperature dependence of equilibrium cyclohexene concentration (initially 5 M) at −45, −63, −77, and −84 °C.

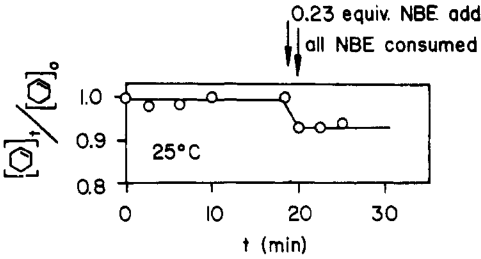

Figure 4. Cyclohexene–norbornene metathesis copolymerization at 25 °C. Initial cyclohexene concentration was 0.1 M; 0.23 equiv of norbornene was added at t = 18 min. Initial tungsten:tin:cyclohexene ratio 1:2.4:5.

Conclusions

Contrary to the reports that cyclohexene is inert to metathesis catalysis, ring-opened products can be obtained under appropriate conditions. At temperatures below −23 °C, an equilibrium mixture of oligomers forms which reverts to cyclohexene upon warming. If the catalyst is destroyed at low temperature, oligomer mixtures can be isolated. Although conversions of cyclohexene are modest at the reaction temperatures employed, the results clearly indicate that, as predicted, suppression of temperature shifts the equilibrium and allows the preparation of metathesis products. Polymerization ceiling conditions were not met and T_c is below −116 °C for 7.5 M cyclohexene. Cyclohexene–norbornene copolymers can be prepared at room temperature; these are kinetic products. The thermodynamic products (cyclohexene and polynorbornene) are obtained at equilibrium; however, the copolymer is stable in the absence of active catalyst and can be isolated.

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Registry No. Polycyclohexene (homopolymer), 25012-94-6; (cyclohexene)·(norbornene) (copolymer), 100207-98-5; tetramethyltin, 594-27-4; tungsten hexachloride, 13283-01-7.

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Chain Flexibility Parameter and Persistence Length of Various Poly(methacrylic acid) Esters

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The theoretical treatments developed by Yamakawa and co-workers on the basis of the wormlike[1] and helical wormlike[2,3] chain models have been frequently used to determine the degree of rigidity of semirigid macromolecules. The latter is expressed by means of the persistence length q, which is conceptually a measure of how far a polymeric chain persists in a given direction. On the contrary, in the case of flexible coils which obey Gaussian statistics, the degree of rigidity is commonly defined by means of the so-called flexibility parameter, which is in fact a measure of the hindrance to internal rotation about the single bonds of the chain.[4] σ represents the ratio $\langle r_0^2\rangle^{1/2}/\langle r_{0,\mathrm{f}}^2\rangle^{1/2}$ of the unperturbed root mean square end-to-end distance $\langle r_0^2\rangle^{1/2}$ to the same distance of a hypothetical chain with free internal rotation $\langle r_{0,\mathrm{f}}^2\rangle^{1/2}$; it ensues that

$$\langle r_0^2\rangle = \sigma^2\langle r_{0,\mathrm{f}}^2\rangle = \sigma^2 n l^2\left(\frac{1+\cos\theta}{1-\cos\theta}\right) \qquad (1)$$

where l is the bond length, θ the supplement of the valence angle, and n the number of bonds. For an infinitely long chain in the coil limit, we have

$$\langle r_0^2\rangle \simeq 2qL \qquad (2)$$

The contour length L is equal to the number of monomer units multiplied by the contribution length of each monomer. It is thus expected from the comparison of eq 1 and 2 that a quadratic dependence of q on σ should be obeyed, as previously mentioned by Kurata and Stockmayer.[4] From a theoretical point of view, comparisons between Flory's rotational isomeric state model and the Kratky–Porod wormlike chain model have been presented by Maedo, Saito, and Stockmayer[5] and by Mansfield.[6] More recently, a detailed comparison between the rotational isomeric state and the helical wormlike cylinder models has been presented by Fujii et al., with particular emphasis on rather flexible chains.[7]

The purpose of the present note is to make use of the Yamakawa–Fujii relationship for the viscosity of wormlike chains to derive values of the persistence length of a series of poly(methacrylic acid) esters (disubstituted asymmetric chains), using experimental results in the ideal Θ state, i.e., in the absence of excluded volume effects. The theory of Yamakawa et al. has been frequently applied to the treatment of the steady-sate transport and dynamic properties of stiff chains such as polynucleotides, polypeptides, cellulose derivatives, poly(n-alkyl isocyanates), etc., but rather less of flexible chains.

Experimental Section

According to Yamakawa and Fujii, the intrinsic viscosity (in $\mathrm{cm^3 \cdot g^{-1}}$) of wormlike chains is related to the molecular weight M and the persistence length q through the relationship

$$[\eta] = \frac{\Phi_\infty M^{1/2}}{(M_L/2q)^{3/2}}\left[1 - \sum_{i=1}^{4} C_i\left(\frac{L}{2q}\right)^{-i/2}\right]^{-1} \qquad (3)$$

where Φ_∞ is the theoretical Flory constant for infinitely large molecular weights (2.87×10^{23} in cgs units) and M_L is the molar mass per unit length, so that $M_L = M/L = M_0/h$ if M_0 and h designate the molecular weight of the monomer and the length of the monomer unit, respectively. C_i are coefficients which depend on the ratio $d/2q$, where d is the diameter of the curved cylinder associated with the wormlike chain. The C_i coefficients can be calculated with the aid of the expressions reported in ref 3 for two $d/2q$ ranges: $d/2q < 0.1$ and $0.1 \leq d/2q < 1.0$. Our calculation procedure consists in fitting the experimental $[\eta]$ vs. M curves with the theoretical equation (3) by means of a multiparametric nonlinear least-squares fitting program.[8] Persistence length and chain diameter are kept as adjustable parameters, whereas the length of the monomer unit, equal to 2.5 Å for a vinylic chain, is considered as a constant. Similar procedures have been already used in the analysis of the viscosity results of cellulose derivatives[9] and polyelectrolytes.[10]

As we detected for some samples $d/2q$ values close to the limit of 0.1, at which the C_i coefficients of eq 3 vary, the fittings were performed for the two situations $d/2q < 0.1$ and $0.1 \leq d/2q < 1.0$. The persistence lengths obtained in this way did not generally differ by more than 4%, and the average of the two q values will be retained for further discussion. On the contrary, the difference in the diameter values can reach a factor of about 2. All the fittings of the experimental data are very close and characterized by relative mean square deviations comprised between 0.01 and 0.02.

Results and Discussion

For some polymethacrylates, Θ conditions were determined experimentally and K_Θ values were directly obtained from the viscosity–molecular weight relationship; the experimental $[\eta]_\Theta$ and $\bar{M}_\mathrm{w}$ values were treated by the computing procedure presented above. For other polymers, intrinsic viscosities were measured in a few good solvents and K_Θ values were calculated with the aid of several theories which imply extrapolations to zero molecular weight: Stockmayer–Fixman, Kurata–Stockmayer, Cowie, Berry, Kamide–Moore, etc. Eight to ten $[\eta]_\Theta,\bar{M}_\mathrm{w}$ pairs were then calculated with the viscosity–molecular weight relationship ($[\eta]_\Theta = K_\Theta \bar{M}_\mathrm{w}^{1/2}$), making use of the mean K_Θ obtained from the various theories. The molecular weight range was between 5×10^4 and 10^6. With the exception

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