The Copolymerization of Cyclic Olefins with Maleic Anhydride*

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Olefins with an internal double bond are known to homopolymerize reluctantly. This is believed to be due to steric interaction, in the propagating transition state, between monomer substituents and the propagating polymer end.[1] It is conceivable that, in addition to steric effects, resonance and polar effects are also operative here, as in the case of vinyl polymerization. The present authors hope to elucidate the reactivities of internal olefins in terms of these and other unknown factors. Cyclic olefins are considered to be simple internal olefins, since both polar and resonance factors can be regarded as constant, with their relative reactivities governed mainly by steric factors.

Some polymerization reactions of cyclic olefins are known. It has been reported that cyclic olefins gave oily low polymers by a radical mechanism under high pressure.[2] Recently, a new type of the ring-opening polymerization of cyclopentene has been reported.[3] As for the copolymerization of cyclic olefins, the formation of polysulfones is a well-known example of radical polymerization.[4] The copolymerization of cyclic olefins with ethylene, using Ziegler catalysts, has also been reported.[5]

The reaction of cyclic olefins with maleic anhydride was reported, by Alder et al.[6] and by Barltrop and Robson[7], to give an 1:1 adduct. More recently, Imoto et al. described the copolymerization of butenes with maleic anhydride.[8]

The present paper will compare the reactivity of cyclic olefins and butene-2 isomers in the copolymerization with maleic anhydride (MAn). The kinetics of the formation of the cyclopentene-MAn copolymer will also be described.

Experimental

Materials. — Cyclobutene was synthesized by the pyrolysis of the adduct of cycloöctatetraene and acetylenedicarboxylic acid according to a known method.[9] The yield of the pyrolysis, which was carried out at 220°C (10 mmHg), was 98%. The infrared spectrum of the product was identical to that reported in the literature.[10] Cyclopentene (b. p. 44—44.5°C), cyclohexene (b. p. 81.5—82.0°C) and cycloheptene (b. p. 115°C) were synthesized by the usual methods. *cis*-Cyclooctene (b. p. 73.5—74.5°C (85 mmHg)) was a commercial product and was purified by rectification. All the monomers were checked for purity by gas chromatography.

MAn was distilled and stored in a desiccator as a benzene solution. 2,2′-Azobis-isobutyronitrile was recrystallized from ethanol.

Polymerization. — Polymerization was carried out in a sealed tube and/or in a dilatometer. Into a 20 ml. glass ampoule was placed a known amount of a monomer solution in benzene, together with an initiator solution. The solution was then degassed, using three freeze-thaw cycles, and sealed under a vacuum, after which the sealed ampoule was kept in a thermostat at 60±0.05°C. In the case of the butenes, a known volume of liquified butene was distilled, under a vacuum, into the ampoule, which contained the other reactants and the solvent. The mixture after polymerization was dissolved in a small amount of dry acetone and reprecipitated with dry ether. This procedure was repeated three times. The polymer was then extracted with ether and dried in vacuo at room temperature.

Dilatometers had a capillary 2 mm. in inside diameter and a total volume of about 13 ml. The volume contraction was read to 10^{-2} mm. by a cathetometer, and the relation between the volume contraction and the conversion was obtained by precipitating the polymer after polymerization.

The Esterification of Copolymers.—When a cyclopentene-MAn copolymer (soft. p. 195—200°C) was refluxed in methanol for 3 days, the result was a homogeneous solution of half esters, which softened at 145—150°C. These half esters were soluble in methanol, acetone and dioxane, but insoluble in ether, benzene, haxane and water. A dioxane solution of the half ester was treated with an ether solution of diazomethane at room temperature to yield the dimethyl esters of the copolymer, which softened at 100—110°C. The dimethyl ester was soluble in acetone and benzene, and insoluble in ether. The infrared spectra of the anhydride copolymer and its dimethylester are shown in Fig. 1.

Found for cyclopentene-MAn copolymer: C, 64.15; H, 6.29. Calcd. for $C_5H_8 \cdot C_4H_2O_3$: C, 65.04; H, 6.06%.

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* Paper V in a series on "The Polymerization of Internal Olefins." For the preceding paper, see *Chem. High Polymers* (*Kobunshi Kagaku*), to be published. Presented at the Meeting of Polymer Science, Kobe, July, 1964.

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Found for dimethyl ester of the copolymer: C, 62.43; H, 7.57. Calcd. for $C_5H_8 \cdot C_6H_8O_4$: C, 62.24; H, 7.59%.

An Analysis of Copolymer Composition.—The copolymers thus obtained were found to have been partly hydrolyzed because of unavoidable contact with moisture, and so the copolymer composition was calculated from an analysis of both carbon and hydrogen, using a calibrated composition formula: $[\text{cycloolefin}]_x [\text{MAn}]_y [H_2O]_z$.

The molecular weight of the copolymers was determined in acetone, and that of the dimethyl ester of the copolymer, in benzene, using a Mechrolab Vapor Pressure Osmometer.

Results

The Reactivity of Cyclic Olefins.—In order to compare the reactivity of cyclic olefins in the copolymerization with MAn, copolymerization was carried out in benzene at an equimolar monomer concentration; the results are shown in Table I.

TABLE I. COPOLYMERIZATION OF CYCLIC OLEFINS (M_2) WITH MAn (M_1)
[MAn] = [Olefin] = 1.54 mol./l.;
[AIBN] = 3.2×10^{-2} mol./l. in benzene; 60±0.05°C

M_2	Time hr.	Yield %	%/hr.	Soft. p. °C	MW
Cyclobutene	0.32	13.2	41.8	180—190	Insol.
Cyclopentene	1.25	26.2	21.0	190—195	1600
Cyclohexene	23	17.7	0.8	170—185	500
Cycloheptene	19	18.3	1.0	240—245	700
Cyclooctene (*cis*)	14	19.7	1.4	250—255	1600

The copolymers obtained in Table I were white brittle solids and were soluble in acetone, dioxane, dimethylformamide, dimethylsulfoxide, pyridine

TABLE II. COPOLYMERIZATION OF CYCLIC OLEFINS (M_2) WITH MAn (M_1) IN BENZENE, 60±0.05°C

M_2	M_1 mol. %	M_2 mol. %	Time hr.	Conversion %	Analysis C, %	Analysis H, %	m_1 mol. %	m_2 mol. %
Cyclobutene	43.8	56.2	0.3	13.2	62.01	5.98	44.4	55.6
	65.0	35.0	0.3	2.2	61.57	5.06	53.7	46.3
Cyclopentene	11.1	88.9	1.1	3.7	64.21	5.81	52.3	47.7
	16.6	83.4	1.2	3.7	64.35	5.97	50.7	49.3
	33.3	66.7	1.5	4.1	64.10	5.93	50.4	48.6
	44.4	55.6	1.7	4.0	63.99	5.99	50.7	49.3
	50.0	50.0	1.9	3.3	63.47	5.97	51.2	48.8
	55.6	44.4	3.3	3.3	63.98	6.01	50.7	49.3
	66.7	33.3	3.4	2.2	62.71	6.09	50.9	49.1
	83.3	16.7	8.5	1.5	62.44	5.85	52.6	47.4
Cyclohexene	33.6	66.4	17.5	6.1	63.94	6.33	54.3	45.7
	50.0	50.0	17.5	10.6	63.34	6.32	54.8	45.2
	66.6	33.4	17.6	9.7	61.82	6.10	57.3	42.7
	80.0	20.0	17.6	9.6	59.72	6.09	58.7	41.3
	83.3	16.7	17.7	11.3	58.20	5.92	61.4	38.6
Cycloheptene	54.0	46.0	15.6	3.4	65.17	6.72	55.6	44.4
	67.4	32.6	15.6	4.9	63.55	6.52	57.8	42.2
	79.2	20.8	15.6	4.4	62.90	6.25	59.8	40.2
	81.0	19.0	15.6	4.0	62.61	6.25	60.0	40.0
Cyclooctene (*cis*)	16.6	83.4	24.4	4.6	67.64	7.60	51.5	48.5
	33.3	66.7	24.4	4.9	66.55	7.34	53.3	46.7
	50.0	50.0	24.5	5.0	65.56	7.17	55.4	44.6
	77.8	22.2	25.3	5.0	63.72	6.97	58.0	42.0
	83.3	16.7	27.0	5.6	62.47	6.98	58.5	41.5
cis-Butene-2	28.5	71.5	14.8	9.2	61.51	6.50	50.2	49.8
	46.6	53.4	14.8	6.3	61.25	6.41	51.2	48.8
	60.8	39.2	14.8	9.0	60.99	6.38	51.2	48.8
	72.2	27.8	14.8	10.7	61.02	6.42	51.2	48.8
trans-Butene-2	28.5	71.5	17.4	5.7	60.67	6.48	50.7	49.3
	46.6	53.4	17.4	4.2	61.04	6.39	51.5	48.5
	60.8	39.2	17.5	4.8	60.81	6.48	51.0	49.0
	72.2	27.8	17.6	4.8	59.98	6.27	52.8	47.2

and methanol (except for the copolymer of cyclobutene), but insoluble in hexane, benzene, chloroform and ether. The cyclobutene copolymer swelled in these solvents. Although a comparison of the relative overall reactivities of cyclic olefins can be made on the basis of these relative rate data, these data do not measure reactivity in propagation because of the inclusion of initiation and termination rates. To obtain a stricter measure of the reactivity in the propagation reaction, monomer reactivity ratios were calculated by the usual procedure from a set of copolymerizations for each monomer. Since cyclic olefins did not homopolymerize under these conditions, the following simplified copolymer composition equation can be used: $(m_1/m_2)-1=r_1M_1/M_2$, where m_1, m_2, M_1 and M_2 denote the concentrations of MAn and cyclic olefin in the copolymer and the monomer mixture respectively. The results are listed in Table II, together with data on butene-2 isomers. The r_1 values are summarized in Table III. The $1/r_1$ value measures the relative reactivity of cyclic olefins towards the MAn radical of the growing polymer end.

TABLE III. MONOMER REACTIVITY RATIOS IN THE COPOLYMERIZATION OF CYCLIC OLEFINS (M_2) WITH (M_1)

M_2	r_1	$1/r_1$
Cyclopentene	0.010 ± 0.003	100
Cyclohexene	0.083 ± 0.005	12
Cycloheptene	0.068 ± 0.002	14.5
Cyclooctene (*cis*)	0.067 ± 0.006	15
cis-Butene-2	0.016 ± 0.005	63
trans-Butene-2	0.030 ± 0.009	33

In calculating the copolymer composition from carbon and hydrogen analysis, a correction was made for the partial hydrolysis of the anhydride group. This treatment was found to give a better straight line with less standard deviation than that which did not consider partial hydrolysis. In fact, the infrared spectra of the copolymers showed a weak shoulder at 1720 cm^{-1} indicating the existence of free acid. Even the same sample yielded different analyses after storage in air, but after correcting for hydrolysis the calculated compositions remained constant.

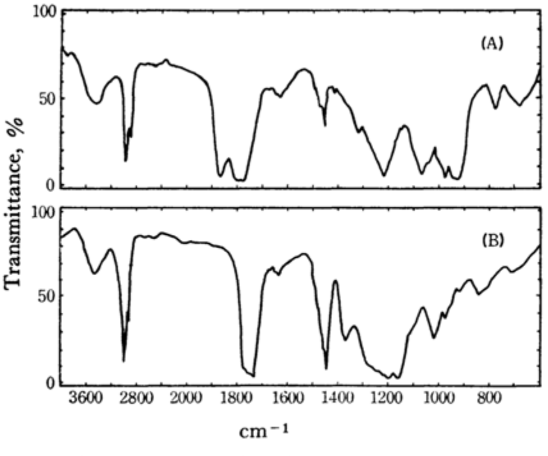

Fig. 1. IR spectra of cyclopentene-MAn copolymer (A), and its dimethyl-esterified product (B).

The copolymer composition curve should go through the point of origin if the simplified copolymer equation represents the system adequately. An intercept at the ordinate might indicate either the existence of a systematic error in the analysis or a penultimate effect.[11] In the present treatment, however, the slope was taken as r_1, with the small intercept at the ordinate ignored.

The data illustrate that *cis*-butene-2 is about twice as reactive as the trans-isomer. The relative reactivity is:

cis/trans = 1.91 from $1/r_1$ values

cis/trans = 1.84 from dilatometric measurements

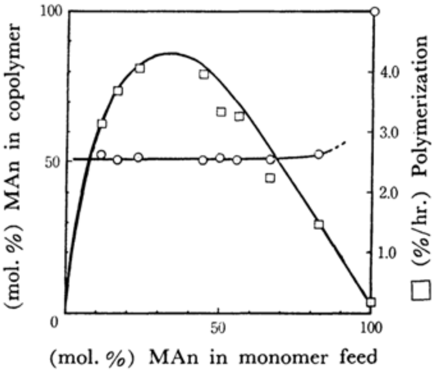

Fig. 2. Copolymer composition and rate in the cycloheptene-MAn copolymerization, 60°C in benzene.
[AIBN] $=1.05\times10^{-2}$ mol. l^{-1}
[MAn+Cyclopentene] $=1.72$ mol. l^{-1}

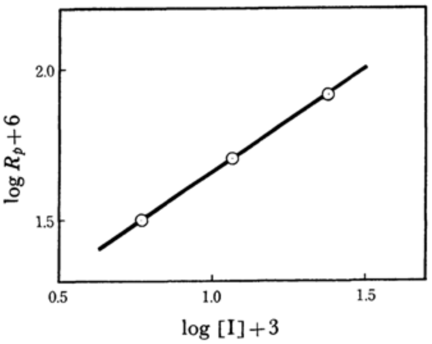

Fig. 3. Dependence of rate on initiator concentration in cyclopentene-MAn copolymerization, at 60°C in benzene.
[MAn] = [Cyclopentene] $=1.186$ mol. l^{-1}

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[11] C. H. Bamford, W. G. Barb, A. D. Jenkins and P. F. Onyon, "The Kinetics of Vinyl Polymerization by Radical Mechanisms," Butterworth Scientific Pub., London (1958), p. 162.

The two values are in good agreement.

The Kinetics of the Cyclopentene-MAn Copolymerization.—The rate data for the copolymerization of cyclopentene and MAn, together with the copolymer composition curve, are shown in Fig. 2. MAn homopolymerizes slightly (0.18%/hr.) under the reaction conditions. A maximum rate was observed at 30 to 40 mol.% of MAn. The dependency of the rate on the initiator concentration (Fig. 3) and on the monomer concentration (Fig. 4) was measured, giving the expression:

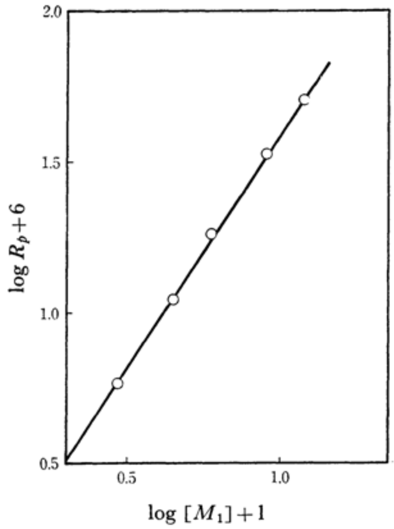

Fig. 4. Dependence of rate on the monomer concentration at 60°C in benzene.
[AIBM] = 1.14 × 10⁻² mol. l⁻¹
[MAn]/[Cyclopentene] = 1

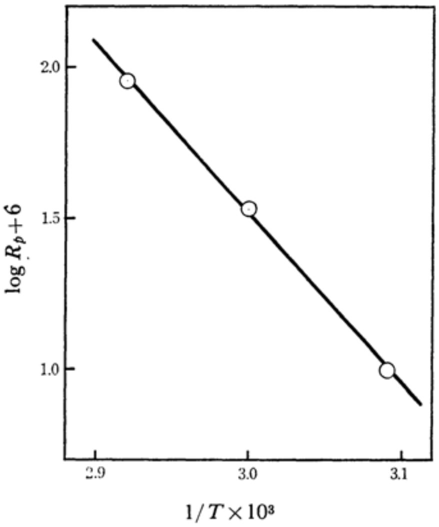

Fig. 5. Dependence of rate on temperature.
[MAn] = [Cyclopentene] = 0.895 mol. l⁻¹
[AIBN] = 1.14 × 10⁻² mol. l⁻¹

$$-(\mathrm{d}M_1+\mathrm{d}M_2)/\mathrm{d}t=k[\mathrm{I}]^{0.68\pm0.005}[\mathrm{M}_1]^{1.54\pm0.018}$$

when $[\mathrm{M}_1]=[\mathrm{M}_2]$

$$k=(8.57\pm0.78)\times10^{-4}\ \mathrm{mol.\ l^{-1}\ sec^{-1}}$$

An Arrhenius plot of the copolymerization rate data (Fig. 5) yielded an overall activation energy of 24.2±0.35 kcal./mol. Thus the overall rate constant, k, at 60°C is:

$$k=Ae^{-E/RT}=5.83\times10^{12}\ e^{-24.2kcal/RT}$$

No thermal polymerization was observed without the initiator for this monomer pair.

The molecular weights of the dimethylated copolymer were measured using a vapor pressure osmometer; values ranged from 3300 to 4400, i. e., the degree of polymerization was 30 to 40. Slight decreases in the molecular weight were observed with increasing monomer concentrations and initiator concentrations.

Discussions

The Copolymers of Cyclic Olefins and MAn.—It may be seen from Table I that cyclobutene is much more reactive than the other cyclic olefins. Although the monomer reactivity ratio was not determined for cyclobutene because of insufficient data, Table II suggests that cyclobutene may add to its own radical. Cyclobutene has not been considered to homopolymerize by a radical mechanism.5) It may also be noted that the copolymer was not soluble, and that even its dimethyl ester only swelled in organic solvents. This fact suggests that cross-linking had taken place during the polymerization, presumably due to opening of the cyclobutene ring.

Upon the dimethylation of the cyclopentene-MAn copolymer, the νC=O band at 1860 and 1780 cm⁻¹ and the δC–O–C band at 1220 cm⁻¹, which are due to the 5-membered cyclic acid anhydride group, disappeared; instead the νC=O of the ester appeared at 1720 cm⁻¹ (Fig. 1). The bands due to the cyclopentane ring at 970 and 920 cm⁻¹ became discernible in the dimethylated copolymer. There was a weak band at 1635 cm⁻¹; the fact that it increased in intensity upon methylation suggests that the νC=C band may be assigned to a double bond of the maleic anhydride type. The formation of that type of unsaturation may result from a chain transfer reaction. It has also been suggested by Joshi that the hydrogen atom of MAn is likely to be abstracted by a radical.12) In fact, the molecular weight of the copolymer is always low, the degree of polymerization being at most 40.

The Copolymerization of MAn (M_1) and Cyclopentene (M_2).—Cyclopentene was chosen as representative of the cyclic olefins, and the kinetics

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12) R. M. Joshi, *Makromol. Chem.*, **53**, 33 (1962).

of its copolymerization were sutdied. The rate of copolymerization was found to be of about the 0.7 th order with respect to the initiator. The value was significantly larger than one half, indicating some contribution of an unimolecular termination to the usual bimolecular one. The degradative chain transfer may partly account for the low molecular weight of the copolymers.

The rate was also found to be of the 1.5th order with respect to the monomer. A theoretical expression for the rate of copolymerization can be reduced to the following simple form in the case of $r_2=0$ and $[M_1]=[M_2]$:

$$R_p=kR_i^{1/2}[M_1]$$

The observed 1.5th order dependency might suggest that the monomer plays a role in the initiation reaction.

The monomer pair was found qualitatively to show a charge transfer band in the ultraviolet absorption spectrum.[13] In such an alternating copolymerization system, a question arises as to whether the two monomers behave as a complexed species in the propagation, as has been suggested in polysulfone formation.[14,15] If so, the rate of copolymerization should be at least of the second-order with respect to the monomer in the above expression, since the concentration of the complex molecule is low enough to be represented by $K_c[M_1][M_2]$. K_c denotes an equilibrium constant of the charge transfer reaction. The observed monomer dependency suggests that the present system is not such an extreme case.

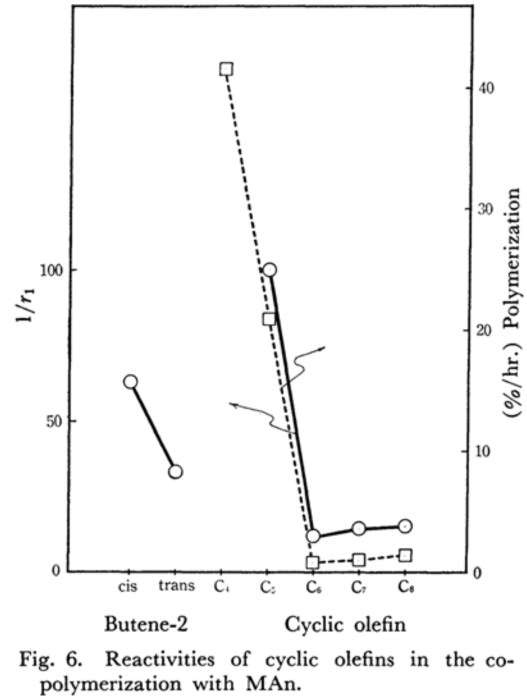

Fig. 6. Reactivities of cyclic olefins in the copolymerization with MAn.

The Reactivity of Cyclic Olefins.—The results listed in Tables I and III are reproduced in Fig. 6. The relative reactivity as determined by the $1/r_1$ value and the rate data are in good agreement. The features may be summarized as: i) The relative reactivities of cyclic olefins towards the growing MAn radical had a minimum at cyclohexene, higher members had slightly higher reactivities, and lower members had markedly higher reactivities.

ii) *cis*-Butene-2 is twice as reactive as the trans-isomer. *trans*-1, 2-Disubstituted ethylenes usually show higher reactivities than the cis-isomer.[16] This was rationalized by assuming that the resonance stabilization of the transition state is favored in the trans-isomers. The explanation could not, however, be applied to the present case.

iii) The reactivities of cyclohexene, cycloheptene and *cis*-cyclooctene were even lower than that of *trans*-butene-2, indicating that ring formation does not always activate the double bond.

The main factors which will control the reactivity of cyclic olefins are considered to be: 1) the difference in the strain energy in an olefin and the corresponding paraffin, 2) the strain energy of olefins, 3) steric hindrance due to ring bulkiness. Factors 1 and 2 will contribute to the activation energy of the propagation reaction, while factor 3 contributes mainly to the entropy term. If it is assumed that there is not much difference in the transition states for all the cyclic olefins, the difference between the strain energy in an olefin and that in the corresponding paraffin might reflect on the activation energy and, hence, on the relative reactivity. The energy difference can be approximated by the heat of the hydrogenation of these olefins.[17] Cyclohexene has the largest heat of hydrogenation, and so it should be the most reactive. However, this was not the case. Thus, factor 1 is not considered to be the predominant one.

A better correspondency was found between factor 2 and the observed reactivity. The strain energy of olefins is reproduced from the literature in Fig. 7.[18] The strain energy of *cis*-butene-2 is larger than that the of trans-isomer, and it is also in good agreement with the observed reactivity. Thus, the strain energy is considered to be one of the main factors which govern the reactivity of cyclic olefins.

Factor 3 may also make some contribution to

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[13] Unpublished data.

[14] W. G. Barb, *Proc. Roy. Soc.*, **A212**, 66 (1952).

[15] I. Ito, T. Saegusa and J. Furukawa, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **65**, 703 (1962).

[16] C. Walling, "Free Radicals in Solution," John Wiley & Sons, New York (1957), p. 127.

[17] J. Gresser, A. Rajbenbach and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 3005 (1961).

[18] J. G. Traynham and M. F. Sehnert, *J. Am. Chem. Soc.*, **78**, 4024 (1956).

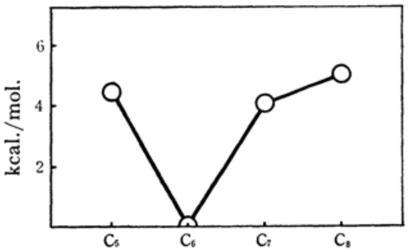

Fig. 7. Strain energy difference of cyclic olefin based on cyclohexene.[18]

the relative reactivity. In a study of methyl affinities,[17] cycloheptene and cyclooctene showed comparable reactivities to cyclopentene. In copolymerization with MAn, the attacking polymer radical is much larger than a methyl radical, and so the steric hindrance of higher cyclic olefins might have been enhanced in the copolymerization.

Summary

The relative reactivities of cyclo-butene, -pentene, -hexene, -heptene, -octene(*cis*), *cis*- and *trans*-butene-2 have been compared in the copolymerization with MAn. The reactivity showed a minimum at cyclohexene, with the higher members having slightly higher reactivities and the lower members having markedly higher reativites than cyclohexene. *cis*-Butene-2 was found to be twice as reactive as the trans-isomer. These facts have been explained by a combination of the effects of the strain energy of olefins and of steric hindrance.

The kinetics of the copolymerization of cyclopentene and MAn was studied at 60°C in benzene, the overall rate being expressed by:

$$R_p=k[\mathrm{I}]^{0.7}[\mathrm{M}_1]^{1.5} \quad \text{when} \quad [\mathrm{M}_1]=[\mathrm{M}_2]$$

$$k=5.83\times 10^{12}\,\mathrm{e}^{-24.2kcal/RT}$$

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