The Effect of Substituents on Ring Size in Cyclopolymerization: An Explanation Based on Frontier Orbital Theory

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ABSTRACT

Fully identified cyclic structures formed via radically initiated cyclizations and cyclopolymerizations are explained using frontier orbital theory. This theory, briefly introduced here for general application to organic polymer chemistry, works very well in explaining the ring size in cyclopolymerization except when steric hindrance is predominant in controlling the course of cyclization.

INTRODUCTION

When a bifunctional monomer undergoes polymerization, a linear polymer is formed. Similarly, a monomer with functionality greater

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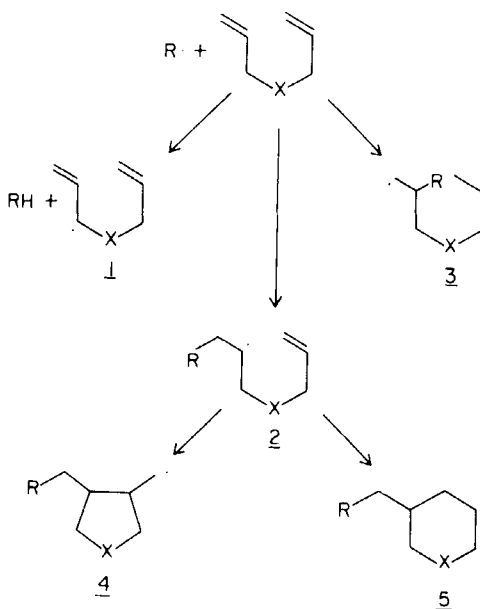
SCHEME 1.

than 2 is expected to give a branched and, ultimately, a cross-linked polymer [1]. This is true in most cases; however, Butler and Ingley [2] showed that under certain conditions 1,6-dienes, monomers with an expected functionality of 4, gave linear polymers which had little or no residual double bond (see Scheme 1). To account for these observations, Butler and Angelo [3] suggested that the propagation reaction involves a series of intramolecular-intermolecular reactions which result in the monomer having an effective functionality of 2. This type of polymerization is now well known as "cyclopolymerization."

Cyclopolymerization has been reviewed in recent years by several authors [4-12], and the broad principles are now well established. However, the structure of the polymer is still not satisfactorily established [13]. The pioneering studies on the structures of the linear polymer derived from 1,6-dienes were concerned with the establishment of the cyclic nature in the repeating units, but the evidence for the structure of the ring was incomplete [13]. This was mainly because of the assumption, considered to be a reliable one based on the known stabilities of radicals (i.e., stability of radicals, 3° > 2° > 1°) [14], that "head-to-tail" propagation would occur in the intramolecular step. Thus, most workers in the field of cyclopolymerization of 1,6-dienes had assumed that a six-membered ring would

be formed. Based on this, the initiating reaction (see Scheme 1) is generally assumed to lead to Radical 2 (and not 1 or 3) and then cyclize to give the secondary Radical 5 (instead of 4). This concept was often not supported by adequate proof of the ring structure. Although many authors challenged that formation of a five-membered ring was also feasible, sufficient evidence to support these arguments was generally not available. However, with the extensive use of ^{13}C-nuclear magnetic resonance (NMR) to aid in identifying the structures of polymers [15, 16] by comparison of their spectra with those of model compounds, and the application of electron spin resonance (ESR) for the study of intramolecular free-radical reactions [17-19], organic chemists are now in a good position to solve the complicated problem of ring size determination and to study the mechanism of cyclopolymerization.

FACTORS WHICH AFFECT THE RING SIZE IN RADICALLY INITIATED CYCLIZATION

While cyclizations of dienes and polyenes through carbonium ion intermediates have been extensively studied with respect to structural and stereochemical parameters, radically initiated cyclizations of dienes have been explored only within the last 10 years. These two processes can differ fundamentally in synthetic results, allowing alternative preferential ring-size formation.
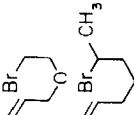
In cyclization of hexa-5-enyl cation 6, six-membered ring 7 is generally obtained. A five-membered ring is formed only when increased electronic stabilization of the carbonium ion intermediate occurs. In contrast, radically initiated cyclizations of hexa-5-enyl Radical 8 generally lead to five-membered ring 9. Six-membered rings can
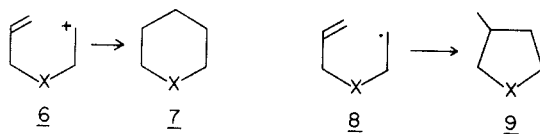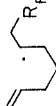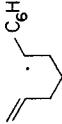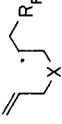
sometimes be obtained as a result of two factors: 1) steric hindrance resulting from bulky groups present on the noncyclized radical center, and 2) electron stabilization of the noncyclized and cyclized radical by electron-withdrawing or conjugating groups. Other minor factors which affect the ring-size distribution in the ring closure products are temperature, polarity of reaction medium, and nature of solvent.

Table 1 lists a number of examples of radically initiated cyclization reactions. Obviously, cyclized products with a five-membered ring are predominant except when the vinyl carbon being attacked or the uncyclized radical is substituted with electron-withdrawing or conjugating groups. Clearly, the transition state is more reactantlike than
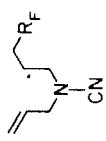
TABLE 1. Radically-Initiated Cyclizations from Hexa-5-enyl Radical

Radical		Ring size of cyclized product 5:6	Ref.
HS⌇ (+ P(OEt))	$\xrightarrow{\text{AIBN}}$ 60°C	43:0	20
Br⌇	$\xrightarrow{\text{DTBP}}$ 120°C	50:3	21
Br⌇—C	$\xrightarrow{\text{AIBN}}$ 30–130°C	78:7	21
		84:0	
		47:0.6	22
Br—CH₃⌇			

X—Y⌇	Peroxide		
X	Y		
H	H	100:0	
H	CN	100:0	
H	$COCH_3$	72:28	
H	$CO_2C_2H_5$	56:44	
$CO_2C_2H_5$	$CO_2C_2H_5$	70:30	
$COCH_3$	$CO_2C_2H_5$	50:50	

Structure	Conditions	Result	No.
	CN CO$_2$C$_2$H$_5$	16:84	
	CN CO$_2$C$_2$H$_5$	0:100	
	(W-Me substituted)		
	BrCl$_3$ AIBN $\longrightarrow$	Predominant	23
R$_I$; R$_F$ = -CF$_2$CF$_2$CF$_3$	+ CCl$_4$		
	CHCl$_3$		
	RS·	Predominant	24
R$_F$; R$_F$ = -CF$_2$CF$_2$CF$_3$	$\overline{\text{R} = \phi, \phi\text{CH}_2\text{-}, \text{CH}_3\text{-}}$		
	R$_1$ = -CO$_2$CH$_3$		
C$_6$H$_5$		80%	25
	T = 70°C	Predominant	26
X; R$_F$ = -CF$_2$CF$_2$CF$_3$	90°C		
X = CH$_2$, O, C(CO$_2$C$_2$H$_5$)$_2$		Only	27

(continued)

TABLE 1 (continued)

Radical		Ring size of cyclized product 5:6	Ref.
(allyloxy radical)	T = 70° C	Only	28
	80° C		
	90° C		
CH_3 radical	40° C	43:1	29
	90° C	30:1	
	125° C	24:1	
C_6H_5 radical	40° C	1:1.82	
	90° C	1:1.92	
	130° C	1:2.0	
allyl N(CN)(R_F) radical		90%	30
$R_F = -CF_2CF_2CF_3$			

$\dfrac{k_1}{k_2} = 43$ at 40°C $\qquad\qquad \dfrac{k_1}{k_2} = 0.55$ at 40°C
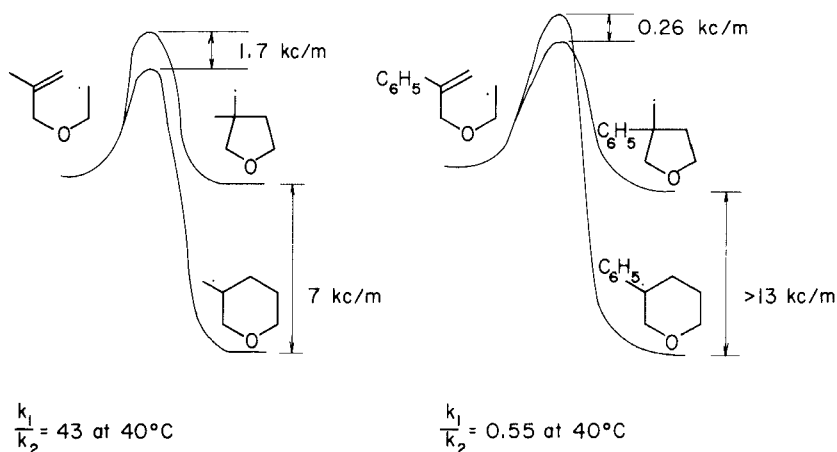
k_1 = rate constant for five-membered ring formation; k_2 = rate constant for six-membered ring formation
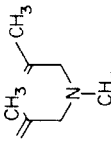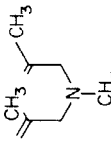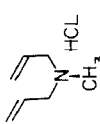
FIG. 1. Reaction coordinates proposed as a result of product distribution study in cyclization of radicals shown [29].
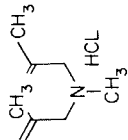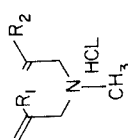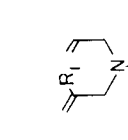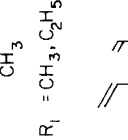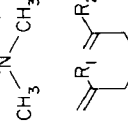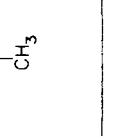
productlike, so the frontier orbital theory can be applied here to explain the cyclization process.

Julia [22, 31, 32] studied cyclization of the 1-substituted 4-hexenyl radical and showed that as substitution in the 1-position by radical stabilizing groups was increased, the mixture of cyclized products changed from nearly pure cyclopentane to cyclohexane derivatives. On this basis it was proposed that the cyclopentane product is the kinetically preferred product, while the cyclohexane product is preferred via thermodynamic control, with the activation energy for cyclization being higher for the cyclohexane derivatives. A more recent study [33] (Fig. 1) has shown that when the radical generated after cyclization of the six-membered ring can be stabilized by resonance, the ratio of six-membered to five-membered rings is markedly increased.

As early as 1959 it was recognized that five-membered rings were formed in competition with the presumably favored six-membered ring [34]. More recently, Brace [30], working with model compounds related to diallylcyanamide, suggested that the five-membered ring structure is preferentially formed in the cyclopolymerization of 1,6-dienes. Recent examinations of the cyclopolymerizations of diallylamines (and their salts, references shown in Table 2) by many authors showed that in most cases five-membered rings are preferred except when steric hindrance from the β-carbon becomes important. In such
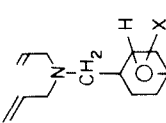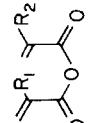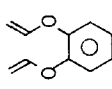
TABLE 2. Cyclopolymerization Studies with Proven Ring Sizes

Monomer	Polymerization conditions	Ring size		Refs.
		Experimental	Predicted	
R = -tBu, -CH$_2\phi$, -ϕ-R', R'= H, -CH$_2$N(CH$_3$)$_2$	TiCl$_3$/H$_2$O$_2$	5 only	5	18, 39
	AIBN, 30°C, or TiCl$_3$/ H$_2$O$_2$	5 only	5	18, 39
	AIBN, 60°C	5 ≈ 6	5	18, 39
	AIBN/30–135°C	$>\dfrac{5{:}6}{10{:}1}$	5	41

Structure	Conditions	Ratio		Ref.
CH_3 , CH_3 , N–CH_3 · HCL, CH_3	AIBN: 30°C 60°C 80°C/1 bar 80°C/8000 bar	5:6 3:2 1:1 7:3 2:3	5	41
R_2 , R_1 , N–CH_3 · HCL, CH_3	AIBN, 60°C: $R_1 = R_2 = C_2H_5$ $R_1 = R_2 = C_6H_5$ AIBN, 30°C: $R_1 = R_2 = CO_2C_2H_5$	 2:3 1:1 <1:100	5 6 6	
R_1 , N–CH_3 $R_1 = CH_3, C_2H_5, C_3H_7$	AIBN, 60°C	5 only	5	42
N^+–CH_3 , CH_3 , CH_3 , Cl^-	Ammonium persulfate	5 only	5	43
R_1 , R_2 , N–CH_3	AIBN, 60°C: R_1 R_2 H H Me H Me Me	5:6 100:0 100:0 30:50	 5 5 5	19, 44

(continued)

TABLE 2 (continued)

Monomer	Polymerization conditions	Ring size		Refs.
		Experimental	Predicted	
Et H		100:0	5	
Pr H		100:0	5	
Bu H		50:50	5	
Ph Ph		50:50	6	
CO_2Et CO_2Et		0:100	6	45
	$TiCl_3/H_2O_2$	5 only	5	
	AIBN, 50°C, 90°C: $R_1 = R_2 = CH_3$, H	6 only	6	46
		6 only	6	
	AIBN, 60°C: $R_1 = H$, $R_2 = CH_3$	6 only	6	
	Benzoyl peroxide, 60°C	6 only	6	47

X, Y - alkyl, e - donating   e - withdrawing

cases, six-membered rings are predominant in the polymer structure. On the other hand, examinations of cyclopolymerizations of acrylic anhydride, methacrylic anhydride, and acrylic methacrylic anhydride still gave predominantly six-membered rings in the polymer structure. All of these observations can be explained fairly well by applying the frontier molecular orbital theory.

SIMPLIFIED FRONTIER ORBITAL THEORY FOR APPLICATION IN ORGANIC POLYMER CHEMISTRY [35, 36]

When two molecules approach each other, their orbitals interact in a manner similar to the formation of a π-bond from isolated p-orbitals. Although the highest occupied molecular orbitals (HOMO's) from both molecules are of comparable energy, their interactions result in an increase in energy. The interaction of the lowest unoccupied molecular orbitals (LUMO's) of both molecules does not lead to stabilization or destabilization. Only the interaction of the HOMO of one molecule with the LUMO of the other molecule gives a stabilization in energy (Fig. 2). The smaller the energy difference in the HOMO of one molecule and the LUMO of the other, the more the interaction is stabilized. Although the interactions of the lower occupied molecular orbitals of one molecule with the higher unoccupied molecular orbitals of the other may cause some stabilization, these effects are much smaller than those caused by HOMO-LUMO interaction. The HOMO and LUMO are the so-called "frontier orbitals."

FIG. 2. The interaction of the HOMO of one molecule with the LUMO of another.
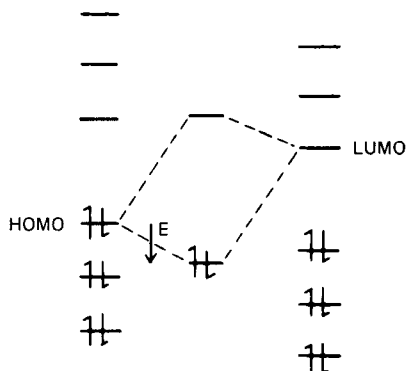
Using perturbation theory, Klopman [37] and Salam [38] derived an expression for the energy gained for lost (ΔE) when the orbitals of one reactant overlap with those of the other:

$$\Delta E = \overset{-\Sigma}{ab}\ (q_a + q_b)\,\beta_{ab}S_{ab} + \underset{k4}{\Sigma}\ \frac{Q_k Q_l}{ER_{kl}} +$$

First term   Second term

$$\underset{r}{\overset{occ.}{\Sigma}}\ \underset{s}{\overset{unocc.}{\Sigma}}\ \underset{s}{\overset{occ.}{\Sigma}}\ \underset{r}{\overset{unocc.}{\Sigma}}\ \frac{Z(\Sigma_{ab}C_{ra}C_{sb}\beta_{ab})^2}{E_r - E_s}$$

Third term

where q_a and q_b are the electron population (electron densities), β and S are the resonance and overlap integrals, Q_k and Q_l are the total charges on atoms k and l, Σ is the total dielectric constant, E_r is the energy of molecular orbital r in the atomic orbitals a and b, R_{kl} is the distance between atoms k and l, and C_{ra} is the coefficient of atomic orbital a in molecular orbital r, where r refers to the molecular orbitals on one molecule and s refers to those on the other. The first term, representing the closed cell repulsion, comes from the interactions of filled orbitals, but this term is neglected in the treatment of frontier orbital theory. This theory is mainly used to explain the features of differential reactivity and will not differ much in either direction if a reaction has a choice of two pathways. The second term is the Coulombic attraction or repulsion and is important only when ionic and/or polar species are reacting together. The third term represents the interactions of all the filled orbitals with all the unfilled orbitals of correct symmetry. This term exists only when $E_r \neq E_s$. So it is the HOMO and the LUMO which are most important. The smaller the value of $E_r - E_s$, the higher the term.

Reactivity is determined by a number of factors, one being the energy of the HOMO. For example, conjugation may make a molecule thermodynamically more stable than an unconjugated one, but it does not follow that conjugated systems are less reactive. They are very often kinetically less stable.

The HOMO of butadiene is ψ_2 (Fig. 3) and that of ethylene is π. The former is higher in energy than the latter, and this leads to its greater activity. Thermodynamic stability is determined by the energies of all
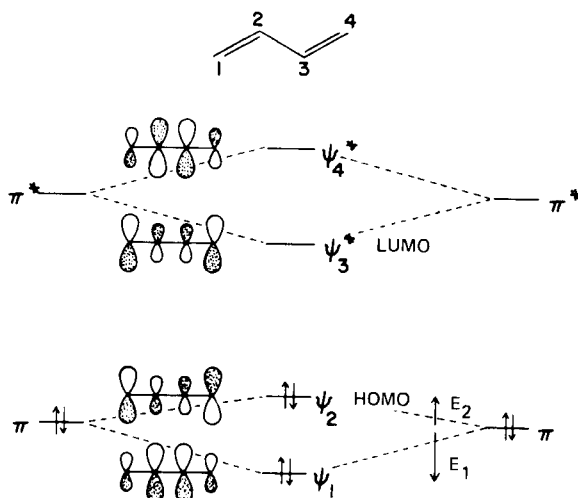
FIG. 3. Energies of the π-molecular orbitals of ethylene and butadiene.

the filled orbitals (ψ_1 and ψ_2), but kinetic stability is mostly (but not exclusively) determined by ψ_2 alone.

Consider an alkene molecule, e.g., a vinyl monomer. When a substituent group is attached to the vinyl carbon, the energy levels of the frontier orbitals are affected. Conjugating substituents (C), like vinyl and phenyl, compress the frontier orbital separation; electron-withdrawing substituents (E), like cyano and carbonyl, lower both frontier orbitals. Since most electron-withdrawing groups are also conjugating in nature, the overall lowering of HOMO is much less than that of LUMO; electron-donating substituents (X), like amino, alkyl, and alkoxyl, raise both frontier orbitals. The related energy levels of frontier orbitals of ethylene and some monosubstituted ethylenes are shown in Fig. 4 for comparison [39]. Here the size of the circle is roughly in proportion to the coefficient on the vinyl carbon in the frontier orbitals; the shaded and unshaded ones are of opposite signs of the coefficient in the molecular orbital representation.

In ionic additions, LUMO's of cation tend to interact more strongly with the HOMO of the vinyl species because of lower energy; similarly, HOMO's of the anion interact more strongly with the LUMO.

In radical additions, the interactions of frontier orbitals, however, are much more complicated. The frontier orbital of a radical is the singly occupied molecular orbital (SOMO). It can interact either with the HOMO or with the LUMO of a vinyl species and gives stabilization
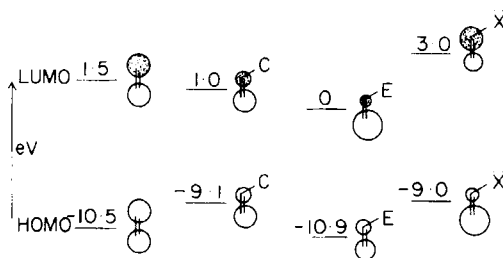
FIG. 4. Frontier orbital energies and coefficients of ethylene and monosubstituted ethylenes.

in energy, although the energy level of the SOMO is closer to the HOMO than to the LUMO in the absence of stronger electron-donating groups. Radicals with a high energy SOMO will react faster with molecules having a lower energy LUMO (Fig. 5a), and radicals with a low-energy SOMO (Fig. 5b) will react faster with a molecule having a high energy HOMO. These kinds of SOMO-HOMO, SOMO-LUMO interactions can be used to explain the course of radically initiated cyclizations in general and radically initiated vinyl polymerization and cyclopolymerization in particular.

In radical additions, the radical will attack on the vinyl carbon with larger coefficient of the appropriate frontier orbital. With C- and E-substituted olefins, the site of attack will be the same regardless of which frontier orbital is more important. Both have higher coefficients on the carbon far from the substituent; for X-substituted olefins, however, the HOMO and LUMO are oppositely polarized. So the radical will attack either vinyl carbon, depending on which frontier orbital is more important.

(a)   (b)

FIG. 5. Important frontier orbital interactions for radicals with high-energy SOMO (a) or low-energy SOMO (b).

For most $\ddot{X}$-substituted olefins, the HOMO will be closer in energy to the SOMO of the radical, because $\ddot{X}$-substituted olefins generally have high energy HOMO's and high energy LUMO's. The reverse addition of radicals to the substituted end of fluoroethylene than to the unsubstituted end is an example:
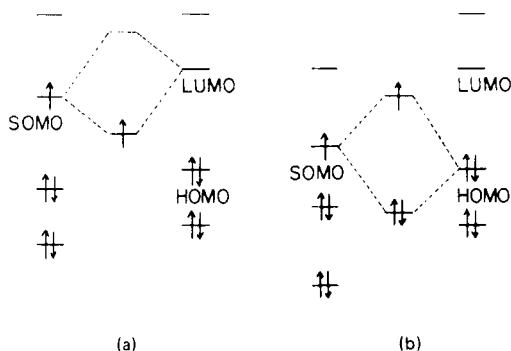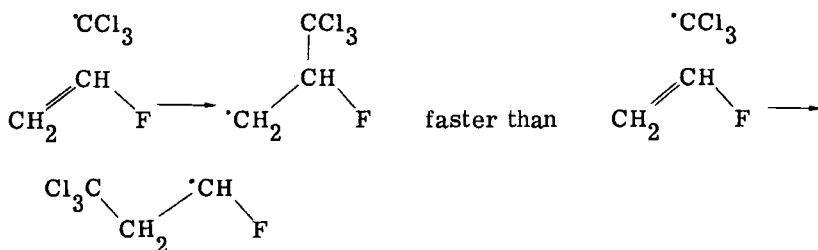

The fluorine is an $\ddot{X}$-substituent as far as the orientation is concerned. Halogens, however, are unusual among the $\ddot{X}$-substituents in that they lower rather than raise the energies of the HOMO and the LUMO. The LUMO of one olefin can become an important frontier orbital, and this orbital has the larger coefficient on the atom bearing the substituent. The chloro-substituent is not quite as effective in lowering the energy of the LUMO, and the HOMO plays an important role in the addition. Another reverse addition is the previously mentioned cyclization of hex-5-enyl radicals [15], where R and R' are electron-withdrawing [31], and addition is thermodynamically [32, 40] controlled. Electron-withdrawing groups give the radical a relatively low energy SOMO, and it will be more sensitive to the polarization of the HOMO of the olefin group. In the radical without electron-withdrawing groups, the interaction with the π-bond will be more affected by the LUMO of the olefin, and this might be part of the reason for contrathermodynamic cyclization:
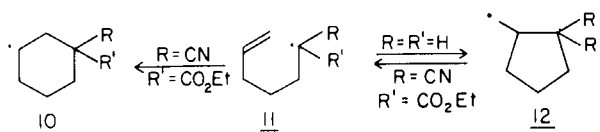
Thermodynamic product   Contrathermo-dynamic product

The above statements can be applied to explanations for the ring sizes of the cyclized products listed in Table 1. In most cases listed in the table, the radical occupies a high energy SOMO (because the carbon bearing the radical is substituted with an electron-donating group), and it will attack the LUMO of the vinyl unit intramolecularly, thereby giving five-membered rings. In other cases, either the radical occupies a low energy SOMO and hence will attack the HOMO

of the vinyl unit or, alternatively, the vinyl unit being attacked is substituted with an electron-withdrawing group and thus has a higher coefficient on the terminal vinyl carbon on both frontier orbitals; hence the radical will attack the terminal carbon, and in these cases six-membered rings are formed.

APPLICATION OF FRONTIER ORBITAL THEORY IN EXPLAINING THE EFFECTS OF SUBSTITUENTS ON THE RING SIZE IN CYCLOPOLYMERIZATION

Although radically initiated cyclopolymerization is somewhat different from the addition of a radical to a double bond intramolecularly or intermolecularly, under proper conditions (i.e., formation of medium-sized rings without much ring strain and in the absence of steric hindrance involved in cyclization) the above arguments on the interactions of the SOMO with the HOMO/LUMO can be used to explain the cyclization process and hence the ring size in radically initiated cyclopolymerization. One important factor in determining the ring size is the interaction of SOMO-HOMO, SOMO-LUMO. Current knowledge about the exact energy level of the SOMO is very limited; hence, a qualitative argument will be adopted. Generally speaking, the energy level of the SOMO is closer to the HOMO than to the LUMO unless strong electron-donating groups are present on the radical center. Table 2 lists a number of examples from recent radically initiated cyclopolymerization studies with adequately substantiated ring sizes. The ring sizes were identified by ^{13}C-NMR (and ESR in some cases; see references in Table 2 for details). The predicted ring sizes (based on frontier orbital theory) are also included for comparison. To illustrate how frontier orbital theory may be applied, two specific examples, both of which are included in Table 2, are examined.

Cyclopolymerization of N-alkyl-diallylamine gives a polymer with five-membered rings. First, the initiating radical which occupies a low energy SOMO attacks the HOMO of the monomer to give the uncyclized Radical 13, which occupies a high energy SOMO. Then it attacks the LUMO of the vinyl unit intramolecularly, as previously discussed, to give the cyclized Radical 14, and this radical, having a low
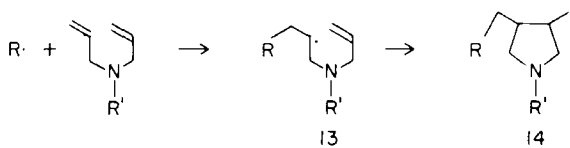

energy SOMO, will then attack the HOMO of another molecule. Propagation then occurs to give a polymer containing only five-membered rings.

Cyclopolymerization of acrylic anhydride gives a polymer contain-ing predominantly six-membered rings [46]. Vinyl units here have a higher coefficient on the terminal carbon of both frontier orbitals, so the radical will attack the terminal vinyl carbon and thus give polymers with consequent head-to-tail propagation. However, the five-membered ring content of polyacrylic anhydride increases with increased solvent polarity, higher polymerization temperature, and reduced monomer concentrations [48].

The ring sizes of cyclopolymers listed in Table 2 can be explained by the above judgments except when bulkiness is developed on a radi-cal center, as in 1) cyclopolymerization of N-methyl-di-(2-ethylallyl)-ammonium chloride, in which six-membered rings are formed, and 2) cyclopolymerization of N-methyl-di-(2-phenylallyl)ammonium chlo-ride, which gives a polymer with ring sizes distributed equally be-tween five- and six-members. Based on frontier orbital theory and steric hindrance arguments, formation of six-membered rings is preferred.

Divinyl ether and maleic anhydride cyclopolymerize radically to give an alternating copolymer of 1 (divinyl ether):2 (maleic anhydride) composition [49]. This polymer has been studied extensively because of its biological activity and antitumor properties. This polymer, like the assignments of ring size in cyclopolymerization studies, was con-sidered to have the [4,3,0] bicyclic structure 15.

15   16
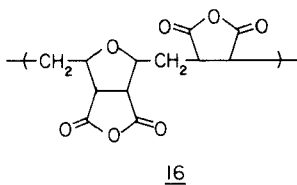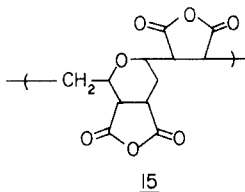
It has recently been shown by ^{13}C-NMR and model compound studies that the copolymer prepared in benzene contains approximately 56% six-membered and 44% five-membered rings [50]. Kunitake and Tsukino [51] argued, based on ^{13}C-NMR studies, that the polymer should have the [3,3,0] bicyclic structure 16 instead of 15. However, a comparative study by Butler and Chu [52] supported a preference for the [4,3,0] bi-cyclic structure by applying high resolution 300 MHz proton NMR on the deuterated and undeuterated polymer. Arguments employing SOMO-HOMO interactions as well as possible participation of a charge-trans-fer complex were cited earlier [52].

Since frontier orbital theory works very well in most radical cy-clization studies, the argument on the ring size of this polymer is well-supported, and the [4,3,0] bicyclic structural unit is believed to pre-dominate in most solvent systems and over a wide temperature range of polymerization. Thus, the following mechanism is supported:
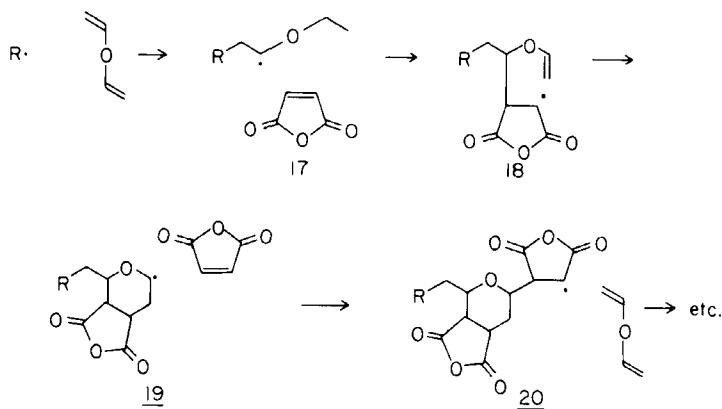
The initiating radical, which occupies a lower SOMO, first attacks divinyl ether (with a high energy HOMO) to give Radical 17 with a high SOMO. This radical then attacks maleic anhydride (with a low energy LUMO) to give Radical 18 with a low energy SOMO, which then attacks the terminal vinyloxy carbon (with a higher energy HOMO and a higher coefficient than the neighboring carbon) to give Radical 19 with a high energy SOMO. Radical 19 then attacks another maleic anhydride molecule to give Radical 20 with a low energy SOMO, etc. The end product is an alternating copolymer containing [4,3 0] bicyclic units. This explanation of alternating cyclopolymerization is exactly the same as that used to explain the alternating copolymerization of vinyl acetate and dimethyl fumarate [53].

CONCLUSION

Frontier orbital theory can be applied to explain the observed ring sizes in cyclopolymerization. Thus, the arguments regarding ring sizes and those in support of the presently accepted mechanism are well documented. In addition, this theory can be applied to explain most vinyl polymerization and copolymerization reactions, and suggests that much of the data on reactivity ratios of certain copolymerizations may need to be reinvestigated. However, a definite problem in full utilization of the frontier orbital theory in organic polymer chemistry is the lack of sufficient information on the energy levels of SOMO's. Therefore, more effort devoted to molecular orbital calculations leading to such information is indicated.

ACKNOWLEDGMENTS

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