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Cyclopolymerization. I. Structure and Mechanism

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Cyclopolymerization. I.
Structure and Mechanism

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ABSTRACT

This paper reviews the subject of cyclopolymerization with emphasis on the reaction mechanism and the structures of the resulting polymers. In general, the structures have been postulated on the assumption that the reaction products are the result of thermodynamic control, no consideration being given to the possibility of kinetic control. Consequently, the majority of polymers are believed to contain six-membered ring units, often with little supporting evidence. The amount of unsaturation present and the number of uncyclized units is also the subject of ambiguous evidence.

THE STRUCTURE OF CYCLOPOLYMERS AND THE MECHANISMS OF THEIR FORMATION

Classical polymer science teaches that when a difunctional* monomer undergoes polymerization, a linear polymer is formed. Similarly, a

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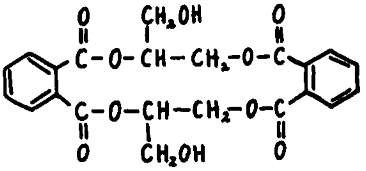
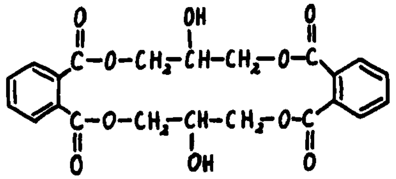
*The functionality of a monomer is defined, in accordance with the concept introduced by Carothers, as the number of other monomers with which it may join when polymerized. [W. H. Carothers, Trans. Faraday Soc., 32, 39 (1936); Chem. Revs., 8, 353 (1931)].

monomer with a functionality greater than two is expected to give a branched and then a cross-linked structure. The theories of Flory [1], Stockmayer [2], and others [3-5] predict the extent of reaction at which cross-linking will occur. In most cases the theoretical predictions approximate to the experimentally observed gel points.

Where discrepancies have arisen between the predicted and observed gel points, various explanations have been offered. For example, when the gel point occurs at a higher extent of reaction than predicted, one explanation has been the loss of functionality as a result of cyclization reactions. A classical example, from step growth polymerization, is the condensation of glycerol with phthalic anhydride where cyclic structures 1 or 2 have been reported [6].



(1)

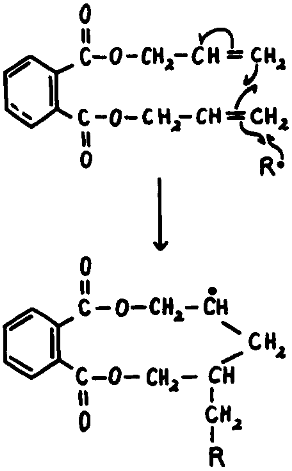


(2)

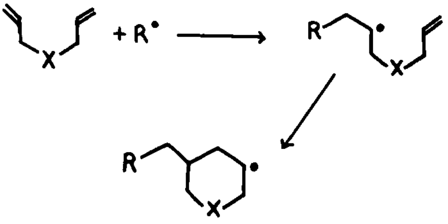
A similar observation was made by Simpson et al. [7-9] in what is presumably a chain polymerization of a tetrafunctional monomer, namely diallyl phthalate.

Simpson et al. proposed structures such as (3) to account for the delay in the gel point. The extreme example of this type of cyclization was reported initially by Butler et al. [10], who showed that, under certain conditions, 1,6-dienes (that is, monomers with an expected functionality of 4) gave linear polymers which were saturated. To account for these observations, Butler [11] suggested that the propagation reaction involved a series of intramolecular-intermolecular reactions which result in the monomer having an effective functionality of 2. This type of polymerization is now generally referred to as cyclopolymerization although the terms intra-intermolecular polymerization [11, 12] and transannular polymerization [13-17] are sometimes used.

Cyclopolymerization has been reviewed by a number of authors [18-24] in recent years and the broad principles are now well established. The propagating species can be an ion or radical and three



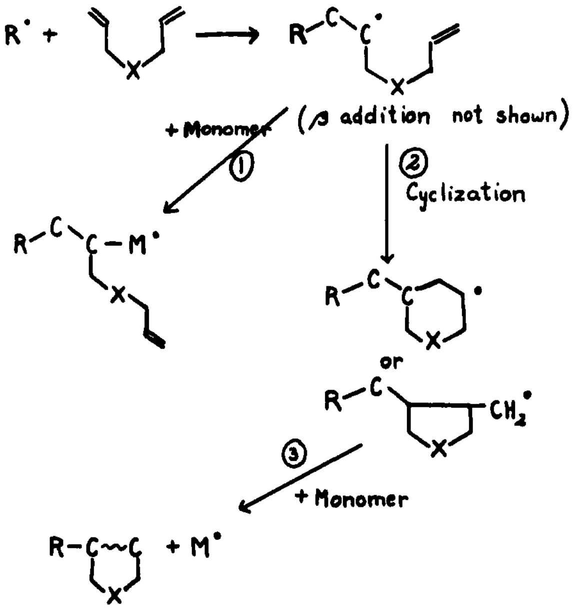
(3)



major reactions compete in the chain growth step (shown here for radical only). These are: 1) the propagation of the uncyclized radical, 2) the cyclization reaction, and 3) attack of the cyclized radical on the monomer.

The relative rates of these reactions depend (among other things) on the experimental conditions and on the structure of the monomer. For example, saturated linear polymers are often formed at low monomer concentrations [11, 25-30] where cyclization (Reaction 2) is favored over propagation of the uncyclized radical (Reaction 1). At higher monomer concentrations the relative ratio of Reactions 1 and 2 can be altered sufficiently to allow for greater amounts of Reaction 1 to occur and the possibility of cross-linked polymer forming [11]. The polymerization of many 1,6-dienes follows this general pattern.

More detailed studies on the structure of the polymers are often lacking or are not sufficiently accurate to support the conclusions reached relating to the proposed structures. Two major points for

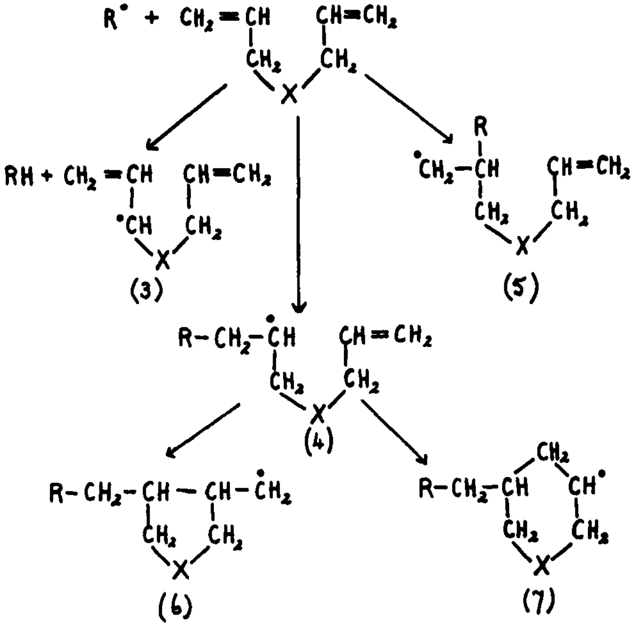


concern are: 1) the size of the ring structures formed in the cyclization step, and 2) the amount, structure, and location of the unsaturated units. An understanding of each of these factors in vital to further developments in cyclopolymerization.

THE RING STRUCTURES FORMED IN CYCLOPOLYMERIZATION

The original studies on the structure of the noncross-linked saturated polymers which were formed from 1,6-dienes were concerned with establishing the cyclic nature of the repeat units and the linear structure of the polymer chains. For example, Butler's [31, 32] degradation studies on the polymer formed from diallylamine hydrobromide established the cyclic nature of the repeat unit but not the size of the ring structures as suggested initially by the authors and by others since. Most, but not all, workers in the field of cyclopolymerization of 1,6-dienes have assumed that six-membered rings would be formed.

The initiating reaction is generally assumed to lead to 4 (and not 3 or 5); with Radical 4 then cyclizing to the secondary Radical 7 (and not 6).



These assumptions are based on generally accepted notions* about the relative stability (thermodynamic) of the radicals; no consideration even being given to their ease and rate of formation (kinetic).

The preconceived idea that the cyclic units are most likely to be six-membered ring structures has often led to inadequate proof of the polymer structure. Many authors have recognized that five- and/or six-membered rings are feasible, but examples are to be found in which proof of structure of the polymer has involved only a comparison of physical properties of the polymer and a six-membered monomeric analog. The possible five-membered monomer analog was not prepared [33]. In the majority of cases, unambiguous proof is difficult to obtain and often only physical evidence is available. In Table 1 [34] are listed the proposed ring units in some cyclopolymerizations and the evidence for the structures proposed; only for a few is the evidence conclusive; e.g., where carbonyl frequency in the IR is well established as being different in a five- or six-membered ring [43].

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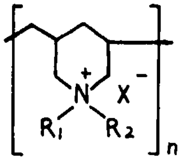
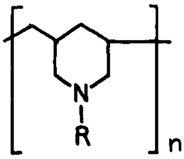
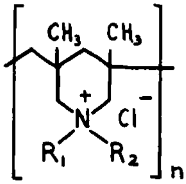
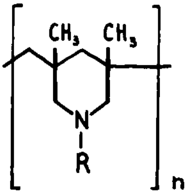
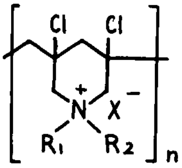
*The relative thermodynamic stabilities of (6) and (7) are difficult to assess a priori, although the common notion would be that (7), being a secondary radical, should be the more stable.

TABLE 1. Evidence for Ring Sizes in Cyclopolymerization

Structure	Evidence[a]	Ref.
		
$R_1 = R_2 = H$; $X = Br$	Sol., IR, Chem.	31
$R_1 = R_2 = H$; $X = Cl$	Sol., IR	31
$R_1 = H$; $R_2 = CH_3$; $X = Cl$	Sol., IR	12
$R_1 = H$; $R_2 = C_2H_5$; $X = Cl$	Sol., IR	12
$R_1 = H$; $R_2 = C_3H_7$; $X = Cl$	Sol., IR	12
$R_1 = H$; $R_2 = C_4H_9$; $X = Cl$	Sol., IR	12
$R_1 = R_2 = CH_3$; $X = Cl$	Sol., IR, Chem.	31, 12, 11
$R_1 = R_2 = CH_3$; $X = Br$	Sol., IR, Chem.	31, 12
$R_1 = CH_3$; $R_2 = CH_2CH_2N^{\oplus}(CH_3)_3$; $X = Cl$	Sol.	35, 36
$R_1 = CH_3$; $R_2 = CH_2CH_2CH_2N^{\oplus}(CH_3)_3$; $X = Cl$	Sol.	35, 36
$R_1 = CH_3$; $R_2 = C_6H_5$; $X = Cl$	Sol.	35, 36
$R_1 = R_2 = C_2H_5$; $X = Cl$	Sol., IR	11
$R_1 = R_2 = C_2H_5$; $X = Br$	Sol., IR	12, 11, 35
$R_1 = R_2 = CH_2CH_2OH$; $X = Cl$	Sol.	35, 36
$R_1 = R_2 = CH_2COCH_3$; $X = Cl$	Sol.	35, 36
$R_1 = R_2 = CH_2CH(NO_2)CH_3$; $X = Cl$	Sol.	35, 36
$R_1 = R_2 = C_4H_9$; $X = Cl$	Sol.	35, 36
$R_1 = R_2 = CH_3OC_6H_5$; $X = Cl$	Sol.	35, 36
$R_1 = R_2 = CH_2CH_2OC_6H_5$; $X = Cl$	Sol.	35, 36
		
$R = SO_3CH_3$	Sol., IR	33, 37
$R = Cl_3CCO$	Sol., IR	38
$R = ClCH_2CO$	Sol., IR	38, 39
$R = CH_2CN$	Sol., IR	39
$R = CN$	Sol., IR	39, 40
$R = CH_3CO$	Sol., IR	38, 39
$R = CH_3OCO$	Sol., IR	39

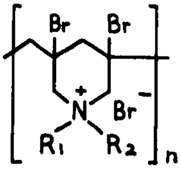
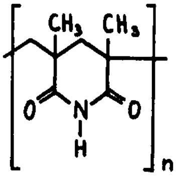
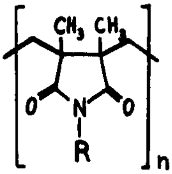
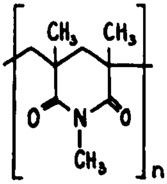
(continued)

TABLE 1 (continued)

Structure	Evidence[a]	Ref.
R = $SO_2C_2H_5$	Sol., IR	33, 37
R = CH_2CH_2CN	Sol., IR	38
R = CH_3CH_2CO	Sol., IR	39
R = $SO_2C_6H_5$	Sol., IR	39
R = $SO_2C_6H_3CH$ - p	Sol., IR	38, 39
R = C_6H_5CO	Sol., IR	38, 39
R = p- $NO_2C_6H_4CO$	Sol., IR	38
R = $CH_2C_6H_5$	Sol., IR	38
		
R_1 = R_2 = H	Sol.	35, 36, 41
R_1 = H; R_2 = CH_3	Sol.	42
R_1 = R_2 = CH_3	Sol.	35, 36
R_1 = R_2 = CH_2CH_2CN	Sol.	35, 36
R_1 = R_2 = $CH_2CH_2CONH_2$	Sol.	35, 36
R_1 = R_2 = cyclopentylmethyl	Sol.	35, 36
R_1 = R_2 = $CH_2CH_2SC_6H_5$	Sol.	35, 36
		
R_2 = SO_2CH_3	Sol., IR	33, 37
R = $SO_2C_2H_5$	Sol., IR	33, 37
		

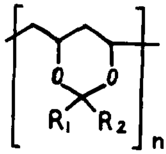
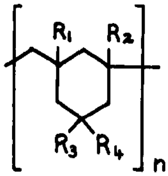
(continued)

TABLE 1 (continued)

Structure	Evidence[a]	Ref.
$R_1 = R_2 = H$; $X = Br$	Sol.	41
$R_1 = R_2 = H$; $X = Cl$	Sol.	41
$R_1 = H$; $R_2 = CH_3$; $X = Cl$	Sol.	41
$R_1 = H$; $R_2 = C_4H_9$; $X = Cl$	Sol.	41
$R_1 = R_2 = CH_3$; $X = Cl$	Sol.	35, 36
		
$R_1 = R_2 = H$	Sol.	41
$R_1 = H$; $R_2 = C_3H_7$	Sol.	41
$R_1 = H$; $R_2 = C_4H_9$	Sol.	41
	Sol., IR, NMR	43, 44
		
$R = CH_3$	Sol., IR, NMR	43, 44
$R = C_2H_5$	Sol., IR	43
$R = C_3H_7$	Sol., IR	43
$R = C_6H_5$	Sol., IR, NMR	43, 44
	Sol., IR	45

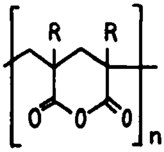
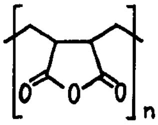
(continued)

TABLE 1 (continued)

Structure	Evidence[a]	Ref.
		
$R_1 = R_2 = H$	Sol., IR, Chem.	46, 47
$R_1 = H; R_2 = CH_3$	Sol., IR, Chem.	46, 47
$R_1 = R_2 = CH_3$	Sol., IR	48
$R_1 = H; R_2 = C_2H_5$	Sol., IR, Chem.	47
$R_1 = CH_3; R_2 = C_2H_5$	Sol.	48
$R_1 = H; R_2 = C_3H_7$	Sol., IR, Chem.	47
$R_1 = H; R_2 = iso - C_3H_7$	Sol., IR, Chem.	47
$R_1 = H; R_2 = C_4H_9$	Sol.	46
$R_1 = H; R_2 = iso - C_4H_9$	Sol., IR, Chem.	47
$R_1 = R_2 = -(CH_2)_5-$	Sol., IR	48
$R_1 = H; R_2 = C_6H_5$	Sol., IR, Chem.	46, 47, 49
$R_1 = H; R_2 = o - CH_3C_6H_4$	Sol., IR, Chem.	49
$R_1 = H; R_2 = m - CH_3C_6H_4$	Sol., IR, Chem.	49
$R_1 = H; R_2 = p - CH_3C_6H_4$	Sol., IR, Chem.	49
$R_1 = H; R_2 = o - CH_3OC_6H_4$	Sol., IR	50
$R_1 = H; R_2 = p - CH_3OC_6H_4$	Sol., IR	50
$R_1 = H; R_2 = m - CH_3OC_6H_4$	Sol., IR	50
$R_1 = H; R_2 = \alpha$-naphthyl	Sol., IR	51
$R_1 = R_2 = C_6H_5$	Sol., IR	51
		
$R_1 = R_2 = R_3 = R_4 = H$	Sol., IR	52
$R_1 = R_2 = R_3 = H; R_4 = Cl$	Sol., IR, Chem.	53
$R_1 = R_2 = R_3 = H; R_4 = OH$	Sol., IR, Chem.	53
$R_1 = R_2 = Cl; R_3 = H; R_4 = COOH$	Sol., IR, Chem.	54
$R_1 = R_2 = R_3 = H; R_4 = COCl$	Sol., IR, Chem.	53
$R_1 = R_2 = R_3 = H; R_4 = CN$	Sol., IR, Chem.	54
$R_1 = R_2 = R_3 = H; R_4 = COOH$	Sol., IR, Chem.	53

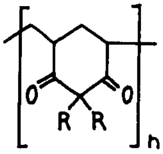
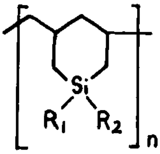
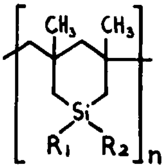
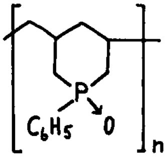
(continued)

TABLE 1 (continued)

Structure	Evidence[a]	Ref.
$R_1 = R_2 = R_3 = H; R_4 = CONH_2$	Sol., IR, Chem.	53
$R_1 = R_2 = CN; R_3 = R_4 = H$	Sol., IR	56, 58
$R_1 = R_2 = H; R_3 = CN; R_4 = COOH$	Sol.	54
$R_1 = R_2 = COOH; R_3 = R_4 = H$	Sol , IR, Chem.	55, 56
$R_1 = R_2 = R_3 = H; R_4 = COCH_3$	Sol.	53, 57
$R_1 = R_2 = R_3 = H; R_4 = COOC_2H_5$	Sol.	53
$R_1 = R_2 = H; R_3 = CN; R_4 = COOC_2H_5$	Sol.	54
$R_1 = R_2 = H; R_3 = R_4 = COCH_3$	Sol.	54
$R_1 = R_2 = COOCH_3; R_3 = R_4 = H$	Sol., IR, Chem.	55
$R_1 = R_2 = Cl; R_3 = COCH_3;$ $R_4 = COOC_2H_5$	Sol., IR	53
$R_1 = R_2 = Cl; R_3 = R_4 = COOC_2H_5$	Sol.	54
$R_1 = R_2 = COOC_2H_5; R_3 = R_4 = H$	Sol., IR, Chem.	55
$R_1 = R_2 = H; R_3 = R_4 = COOC_2H_5$	Sol., IR	57
$R_1 = R_2 = H; R_3 = C_6H_5; R_4 = CN$	Sol.	53
$R_1 = R_2 = R_3 = H; R_4 = COOC_6H_5$	Sol.	53
$R_1 = R_2 = R_3 = H; R_4 = OCOC_6H_5$	Sol.	53
$R_1 = R_2 = R_3 = H; R_4 = CONHC_6H_5$	Sol.	53
$R_1 = R_2 = C_6H_5; R_3 = R_4 = H$	Sol., IR	59
$R_1 = R_2 = COCl; R_3 = R_4 = H$	Sol.	58
$R_1 = R_2 = CONH_2; R_3 = R_4 = H$	Sol., IR	56, 58
$R_1 = R_2 = H; R_3 = COCH_3; R_4 =$ $COOC_2H_5$	Sol., IR	57
		
$R = H$	Sol., IR, Chem.	60, 61, 32
$R = CH_3$	Sol., IR, Chem.	62, 63, 64
	Sol., IR	61

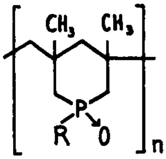
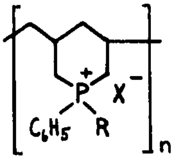
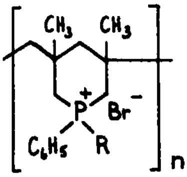
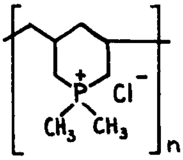
(continued)

TABLE 1 (continued)

Structure	Evidence[a]	Ref.
		
R = H	Sol., IR	65
R = CH_3	Sol., IR	66
		
R_1 = H; R_2 = CH_3	Sol., IR	67
R_1 = H; R_2 = C_2H_5	Sol., IR	67
R_1 = H; R_2 = C_6H_5	Sol., IR	67
R_1 = R_2 = CH_3	Sol., IR	67, 68
R_1 = R_2 = C_2H_5	Sol.	67
R_1 = CH_3; R_2 = C_6H_5	Sol., IR	67, 69, 28
R_1 = R_2 = C_6H_5	Sol., IR	68
R_1 = R_2 = $-(CH_2)_4-$	Sol., IR	28
R_1 = R_2 = $-(CH_2)_5-$	Sol., IR	28
		
R_1 = R_2 = CH_3	Sol., IR	28
R_1 = R_2 = C_6H_5	Sol., IR	28
R_1 = CH_3; R_2 = C_6H_5	Sol., IR	28
R_1 = R_2 = $-(CH_2)_5-$	Sol., IR	28
	Sol., IR	30, 70

(continued)

TABLE 1 (continued)

Structure	Evidence[a]	Ref.
		
R = CH_3	Sol., IR	71
R = C_2H_5	Sol., IR	71
R = C_6H_5	Sol., IR May contain five-membered rings	30
		
R = CH_3; X = Br	Sol., IR	27
R = C_2H_5; X = Br	Sol., IR	27
R = C_3H_7; X = Br	Sol., IR	27
R = C_6H_5; X = Br	Sol., IR	27
R = C_6H_5; X = Cl	Sol., IR	27
		
R = CH_3	Sol., IR	27
R = C_2H_5	Sol., IR	27
R = C_3H_7	Sol., IR	27
R = C_6H_5	Sol., IR	27
	Sol., IR	27

[a] Sol. = solubility; IR = infrared; NMR = nuclear magnetic resonance; Chem. = chemical.

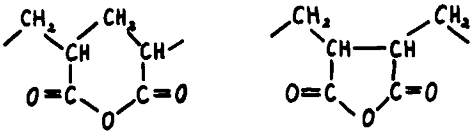
In a number of model 1,6-diene systems, cyclization of radicals of Type 4 has been demonstrated to give five-membered rings [72-75]. Some authors have expressed surprise [26] that the reactions should proceed via Radical 6. This is a direct result of placing too much emphasis on the stability of the final radical (see preceding footnote) or product at the expense of considering the likely transition states and the relative rates of the competing reactions.

Radical addition to a carbon-carbon double bond has been suggested [76-79] to proceed via the following transition states, but to conclude which of these states applies to cyclopolymerization is not possible at present.

However, in any case, given that there is a preferred transition state, it is reasonable to expect different rates of cyclopolymerization leading to five- or six-membered rings.

Where Radical 6 is formed more rapidly than Radical 7, formation of five-membered ring products is expected though their formation involves a primary radical.

The situation could be complicated further by the formation of both five- and six-member rings, and by a change in ring size with reaction conditions, as evidenced by the studies of Smets [61] and Butler [44].



THE RESIDUAL UNSATURATION IN CYCLOPOLYMERS

The residual unsaturation, if any, in cyclopolymers is important from the point of view of the propagation and termination reactions and the practical aspects of the properties of the polymer.

Knowledge of the number of residual double bonds in conjunction with the chain length is a measure of the relative rates of cyclization (Reaction 2) and propagation of the noncyclized radical (Reaction 1). As mentioned above, the concentration of the monomer has a bearing on the relative rates of these reactions and hence on the formation, either during polymerization or subsequently, of a cross-linked structure.

The location of the noncyclized units is important as they are possible chain transfer and chain terminating agents [60].

From the practical viewpoint, polymers with a cross-linked or potentially cross-linked structure (i.e., those which contain some unsaturation) and those with a saturated linear structure would have vastly different applications and processing characteristics.

The accurate measurement of residual unsaturation by chemical methods is difficult [80], and most results have been obtained by physical methods [34, 44] (Table 1). The inherent accuracy of these physical methods, however, is not good enough to give the information required.

Overriding the problems of measurement of unsaturation is the difficulty of isolating the polymer, free from monomer, in a manner which does not destroy the unsaturated centers. For example, Butler [81] has shown that prolonged extraction of polydiallylammonium chlorides reduced the unsaturation from 7.5 to 5.5%. While Butler concluded that this was evidence for monomer occlusion, the results support equally well the loss of unsaturation by oxidation or some other chemical transformation.

SUMMARY

1,6-Dienes have been shown to yield polymers which contain five, six, and a mixture of five- and six-membered rings (in different chains?). The polymers may contain noncyclized unsaturated units and be essentially linear, or the unsaturated centers may undergo further reaction to give cross-linked polymers.

Much of the evidence for the polymer structures proposed is ambiguous, and further detailed studies are necessary to establish specific polymer structures conclusively. This is a complicated problem since one polymer chain may contain all possible structures, and it is likely that the chain ends could be different from the main structural units. For example, it is feasible that the main chain repeat unit could be a five-membered ring and the terminal unit a six-membered ring or a noncyclized unit.

The papers that follow in this symposium will attempt to answer some of the questions posed above with specific emphasis on diallylamine-type monomers.

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