Cyclopolymerization

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1 Introduction

During a study of the polymerization of quaternary ammonium salts containing allyl groups, undertaken to prepare polymers for use as ion-exchange resins, Butler and co-workers at the University of Florida found that insoluble polymers were only obtained from monomers containing three or four allyl groups. Polymers from diallyl quaternary ammonium salts were completely soluble in water, and therefore not cross-linked, and contained no residual unsaturation.

These results were contrary to the accepted view that monomers with two non-conjugated double bonds give polymers which are *either* cross-linked, insoluble, and largely saturated *or* linear, soluble, and containing approximately one residual double bond for each repeating unit.

To explain the formation of soluble, linear polymers from diallyl quaternary ammonium halides, a chain-growth mechanism was proposed which involved alternating intramolecular and intermolecular steps.[1] This mechanism, Scheme 1, is now known as cyclopolymerization.

To confirm the proposed structure, representative polymers were degraded and products were obtained which were explained by assuming a cyclic unit.[2] Poly(diallylammonium bromide) (1) was degraded as shown. Poly(diallyldimethylammonium bromide) was degraded by the exhaustive methylation method (4)—(7).

Although before Butler's work the polymerization of non-conjugated dienes always eventually led to insoluble cross-linked products, the possibility of some cyclization occurring had been recognized. Simpson *et al.*[3] showed that cyclic structures were present to the extent of approximately 41% in the polymers of diallyl phthalate, and later observed,[4] during the formation of cross-linked polymers from fourteen diallyl esters, that some intramolecular reaction occurred in all cases.

Since these initial investigations, it has been shown that cyclopolymerization can occur almost quantitatively in a wide variety of symmetrical dienes which can cyclize to form a five- or six-membered ring structure, a favourable reaction for both kinetic and thermodynamic reasons. Other studies have demonstrated that cyclic units in a polymer chain can be obtained from unsymmetrical non-

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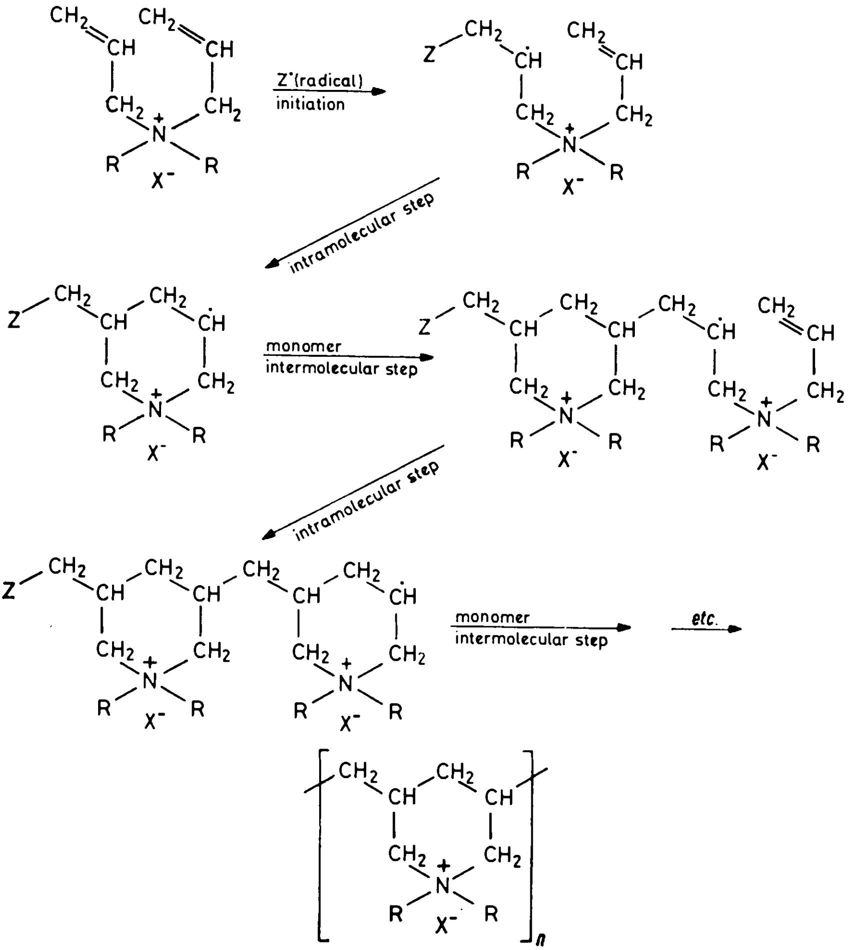
[1] G. B. Butler and R. J. Angelo, *J. Amer. Chem. Soc.*, 1957, **79**, 3128.

[2] G. B. Butler, A. Crawshaw, and W. L. Miller, *J. Amer. Chem. Soc.*, 1958, **80**, 3615.

[3] W. Simpson, T. Holt, and R. J. Zetie, *J. Polymer Sci.*, 1953, **10**, 489.

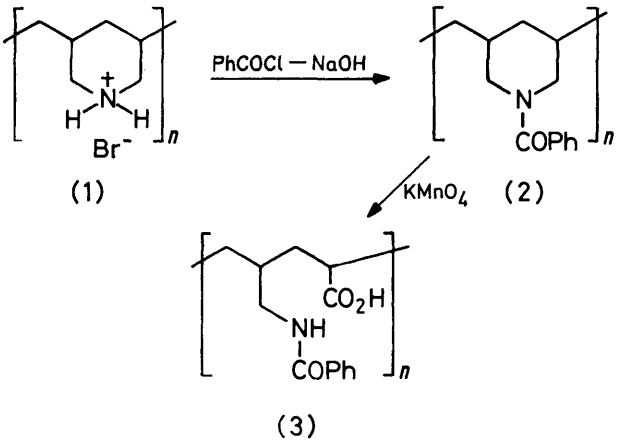
[4] T. Holt and W. Simpson, *Proc. Roy. Soc.*, 1956, **A238**, 154.

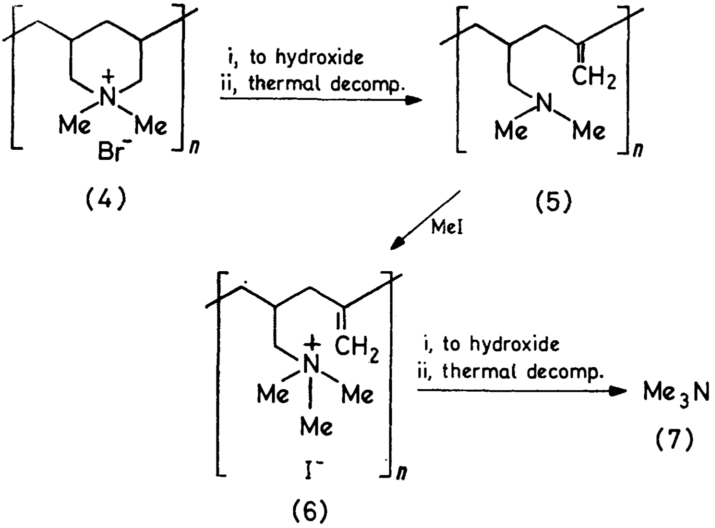


Scheme 1

conjugated dienes and from monomers containing other polymerizable groups. It has been established that polycyclic units can form by a succession of ring closures within a monomer molecule, by transannular polymerization or, in the polymerization of 1,4-dienes, by interaction of two monomer molecules. Copolymerization of certain monomers can lead to cyclic structures in the polymer chain in which both co-monomers are involved.

This review will indicate the scope of the cyclopolymerization mechanism as a means of synthesizing linear polymers containing cyclic structures in the main chain. The homopolymerization and copolymerization of a wide variety of





monomers will be briefly discussed. A review dealing with the kinetics and mechanism of cyclopolymerization has been published[5] and an exhaustive review on cyclopolymerization is in preparation.[6]

Most of the work on cyclopolymers has been carried out in the U.S.A., the U.S.S.R., and Japan. Much of the interest in this method of producing polymers

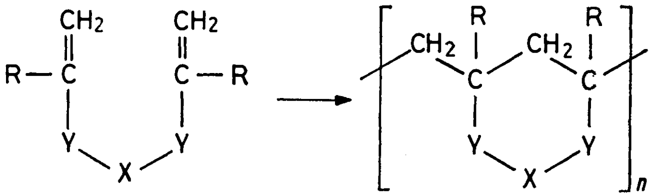
[5] W. E. Gibbs and J. M. Barton, in 'Kinetics and Mechanism of Polymerization', ed. G. E. Ham, Dekker, New York, 1967, Vol. 1, Part 1. Chap. 2.

[6] G. B. Butler, G. C. Corfield, and C. Aso, 'Progress in Polymer Science', ed. A. D. Jenkins, Pergamon, London, to be published.

with cyclic structures in the main chain arose from the search for thermally stable polymers. Although no outstanding results have been achieved in this direction, polymers with other valuable properties have been discovered and a range of cyclopolymers is produced commercially in the U.S.A.

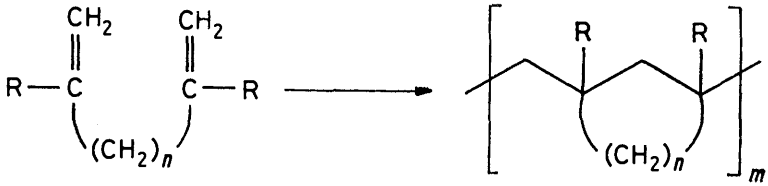
2 Cyclopolymerization of Non-conjugated Dienes

A. Polymerization of Symmetrical 1,5- and 1,6-Dienes.—After Butler's initial investigations, it was soon demonstrated that a variety of symmetrical 1,5- or 1,6-dienes could be polymerized to soluble saturated polymers, and structures were proposed in which five- or six-membered rings, respectively, alternated with methylene groups along the linear chain. For symmetrical 1,6-dienes (8), structure (9) has been proposed.



(8) (9)

Marvel and co-workers[7] found that soluble polymers were obtained from the polymerization of hexa-1,5-diene, hepta-1,6-diene, and related compounds (10). Carbocyclic structures (11) were proposed and partial dehydrogenation of some of the 1,6-diene polymers, using potassium perchlorate at high temperatures, gave products showing the i.r. and u.v. spectral characteristics of *meta*-substituted aromatic rings.



(10) $n = 2$; $R = H, Me, CO_2Me$, or Ph
$n = 3$; $R = H, CO_2H, CO_2Me, CO_2Et, CN$, or Ph

(11)

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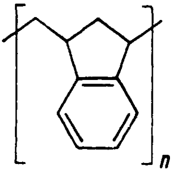
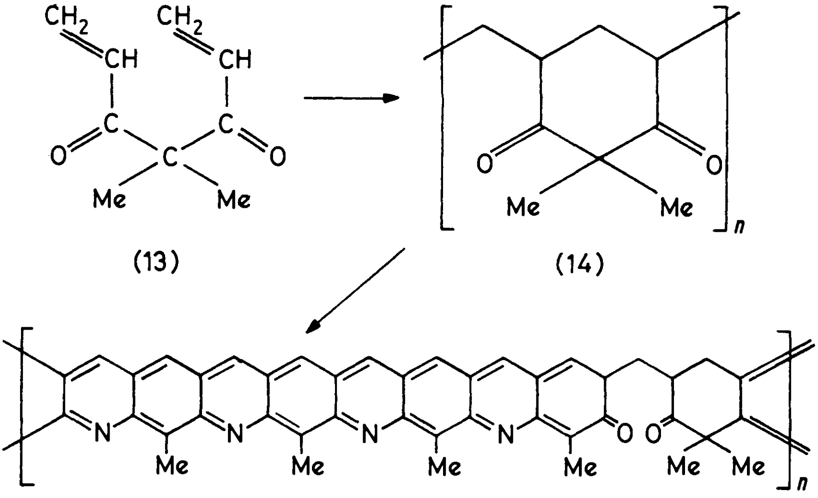
[7] C. S. Marvel and R. D. Vest, *J. Amer. Chem. Soc.*, 1957, **79**, 5771; 1959, **81**, 984; C. S. Marvel and J. K. Stille, *ibid.*, 1958, **80**, 1740; C. S. Marvel and E. J. Gall, *J. Org. Chem.*, 1960, **25**, 1784.

Aso and co-workers[8] have investigated the polymerization of *o*-divinylbenzene in some detail. Under a variety of conditions, using free-radical, cationic, and anionic initiators, soluble polymers with a low residual double-bond content were obtained. It was concluded that *o*-divinylbenzene is converted into a linear polymer having five-membered ring units in the main chain formed through a cyclopolymerization mechanism (12).



(12)

4,4-Dimethylhepta-1,6-diene-3,5-dione (13) gave a soluble cyclopolymer (14) from which a mono-oxime (90% oximated) was obtained. This mono-oxime yielded[9] a ladder polymer (15), with good thermal stability, *via* a Knoevenagel reaction.



(13) (14)

(15)

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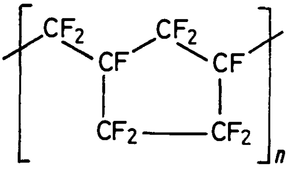
[8] C. Aso, T. Nawata and H. Kamao, *Makromol. Chem.*, 1963, **68**, 1; C. Aso and R. Kita, *Kogyo Kagaku Zasshi*, 1965, **68**, 707; C. Aso, T. Kunitake and R. Kita, *Makromol. Chem.*, 1966, **97**, 31; C. Aso, T. Kunitake, Y. Matsugama, and Y. Imaizumi, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1968, **6**, 3049; C. Aso, T. Kunitake, and Y. Imaizumi, *Makromol. Chem.*, 1968, **116**, 14.

[9] W. DeWinter and C. S. Marvel, *J. Polymer Sci., Part A*, 1964, **2**, 5123.

Saturated polymers have been obtained from perfluorohexa-1,5-diene, perfluorohepta-1,6-diene and 4-chloroperfluorohepta-1,6-diene at high temperature and pressure by irradiation from cobalt-60. The polymer structures (16)—(18) were proposed.[10]



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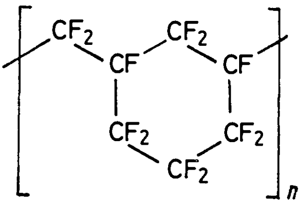

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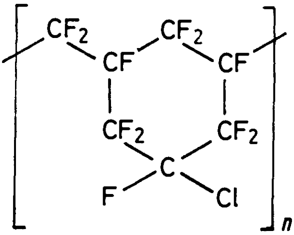

(18)

Although a six-membered ring has been proposed as the main unit in the structure of cyclopolymers from 1,6-dienes,[1,2,7,9,10] two different cyclic structures are possible, containing either a five- or a six-membered ring, depending on the orientation of the second double bond at the intramolecular propagation step. However, in only a few cases has the precise nature of the cyclic recurring unit been adequately demonstrated.

Sultanov and Arbuzova[11] found that the polymerization of divinyl acetals (19) produced poly(vinyl acetals) containing both five- and six-membered ring structures, (20) and (21) respectively.

Poly(vinyl acetals) are generally prepared by the acid-catalysed condensation of poly(vinyl alcohol) with aldehydes. Complete acetal formation does not take place since hydroxy-groups become isolated and cannot form a cyclic acetal.

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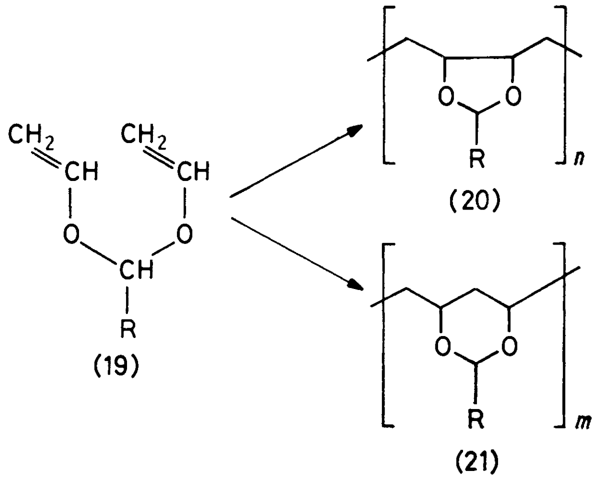
[10] D. W. Brown and L. A. Wall, *J. Polymer Sci., Part A-2, Polymer Phys.*, 1969, **7**, 601.

[11] I. A. Arbuzova and K. Sultanov. *Vysokomol. Soedinenii*, 1960, **2**, 1077; K. Sultanov and I. A. Arbuzova, *Uzbek. Khim. Zhur*, 1963, **7**(2), 57; 1963, **7**(4), 58; 1965, **9**(6), 38.


(19)
(20)
(21)

Matsoyan and co-workers[12] demonstrated that complete acetals of poly(vinyl alcohol) can be obtained directly from monomers by the cyclopolymerization of divinyl acetals and a wide variety of poly(vinyl acetals) have been prepared by this method.[11,12] Polymerization using radical initiators occurs exclusively by the cyclopolymerization mechanism, even in bulk. Using ionic initiators, aromatic divinyl acetals gave linear cyclopolymers containing no residual unsaturation. The polymerization of aliphatic divinyl acetals, however, resulted in soluble polymers with some pendant vinyl groups. The ionic polymerization of divinyl formal gave only cross-linked polymer under a variety of conditions. To determine the average frequency of each type of cyclic unit, a series of poly(divinyl acetals) were hydrolysed and the resultant poly(vinyl alcohols), containing 1,2- and 1,3-glycol units, from five- and six-membered rings respectively, analysed. The results gave $n : m = 23 : 77$ and were independent of R.

The polymerization of acrylic anhydride and methacrylic anhydride has been exhaustively studied.[13] High yields of polymer have been obtained in bulk or

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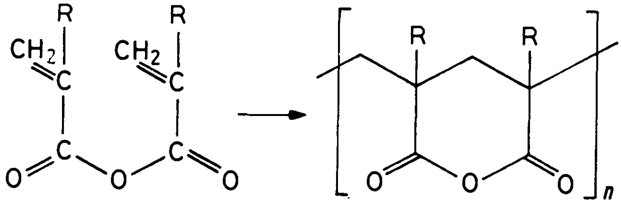
[12] S. G. Matsoyan and M. G. Avetyan, *Zhur. obschei Khim.*, 1960, **30**, 697; S. G. Matsoyan, *J. Polymer Sci.*, 1961, **52**, 189; S. G. Matsoyan, M. G. Avetyan, and M. G. Voskanyan, *Vysokomol. Soedinenii*, 1961, **3**, 562; S. G. Matsoyan, M. G. Avetyan, L. M. Akopyan, M. G. Voskanyan, N. M. Morlyan and M. A. Eliazyan, *Vyosokomol. Soedinenii*, 1961, **3**, 1010; S. G. Matsoyan, M. A. Eliazyan, and E. Ts. Gevorkyan, *Vysokomol. Soedinenii*, 1962, **4**, 1515; S. G. Matsoyan and M. G. Voskanyan, *Izvest. Akad. Nauk Arm. S.S.R., Khim. Nauki*, 1963, **16**, 151; S. G. Matsoyan, M. G. Voskanyan, and A. A. Saakyan, *Izvest. Akad. Nauk Arm. S.S.R., Khim. Nauki*, 1963, **16**, 455; S. G. Matsoyan and L. M. Akopyan, *Vysokomol. Soedinenii*, 1961, **3**, 1311; 1963, **5**, 1329; S. G. Matsoyan, G. M. Pogosyan, and A. A. Saakyan, *Vysokomol. Soedinenii*, 1963, **5**, 1334; S. G. Matsoyan and L. M. Akopyan, *Izvest. Akad. Nauk Arm. S.S.R., Khim. Nauk*, 1963, **16**, 51.

[13] A. Crawshaw and G. B. Butler, *J. Amer. Chem. Soc.*, 1958, **80**, 5464; J. F. Jones, *J. Polymer Sci.*, 1958, **33**, 15; G. V. D. Tiers and F. A. Bovey, *ibid.*, 1960, **47**, 479; W. L. Miller, W. S. Brey, jun., and G. B. Butler, *ibid.*, 1961, **54**, 329; J. Mercier and G. Smets, *ibid.*, 1962, **57**, 763; W. E. Gibbs and J. T. Murray, *ibid.*, 1962, **58**, 1211; J. C. H. Hwa, *ibid.*, 1962, **60**, S12; J. C. H. Hwa, W. A. Fleming, and L. Miller, *J. Polymer Sci., Part A*, 1964, **2**, 2385.

solution polymerizations using radical initiators. Methacrylic anhydride yielded soluble polymers in all cases except at high monomer concentration and high conversion in polar solvents. Soluble polymers from acrylic anhydride were only obtained by solution polymerization. The amount of residual unsaturation in these polyanhydrides was small but was greater in poly(acrylic anhydride) than in poly(methacrylic anhydride). Clearly linear polyanhydrides with recurring cyclic anhydride units are obtained by a cyclopolymerization mechanism, (22)→(23). The i.r. spectra of the polymers exhibited carbonyl absorption bands characteristic of six-membered cyclic anhydrides.



(22) R = H or Me (23)

Crawshaw and Butler showed that poly(acrylic acid) obtained by the hydrolysis of poly(acrylic anhydride) was substantially more crystalline than conventional poly(acrylic acid). Thus there may be some stereoregulating influence in the cyclopolymerization mechanism.

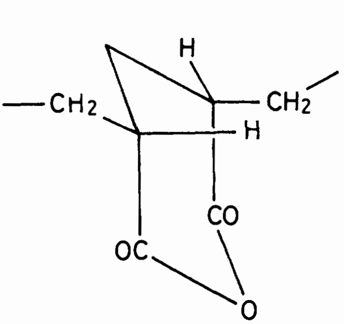
From a comparison of the i.r. spectra of poly(acrylic anhydrides) and the optical isomers of $\alpha\alpha'$-dimethylglutaric anhydride, Mercier and Smets discovered the existence of two stereoisomeric types of structural unit (24) and (25). The less stable anhydride unit [syndiotactic, (24)] is formed more easily (kinetic product) but, owing to the possibility of enolization, isomerizes to the thermodynamic product [isotactic, (25)] in a catalytic solvent or at high polymerization temperature.

A polymer with a relatively high content of five-membered anhydride structural units has been obtained by polymerization of acrylic anhydride at 115 °C in xylene.

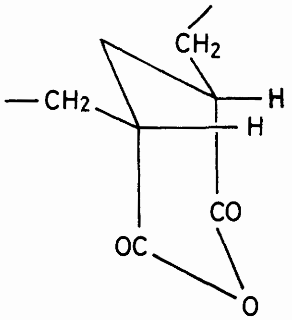
The stereochemical configuration of poly(methyl methacrylate) derived from the cyclopolymer poly(methacrylic anhydride) has been investigated by n.m.r. spectroscopy. The results indicate that some regulation of the stereochemical configuration does occur. The polymers are mainly composed of a random arrangement of syndiotactic (+ − + − + − + −) and heterotactic (+ + − − + + − −) blocks of various lengths, such as:

+ − + − − + + − − + + − − + − + − + − + + −

There were no consecutive isotactic units greater than two in a polymer prepared at −50 °C, but there was a definite increase in the isotactic character with an increase in polymerization temperature. Here too the syndiotactic structure



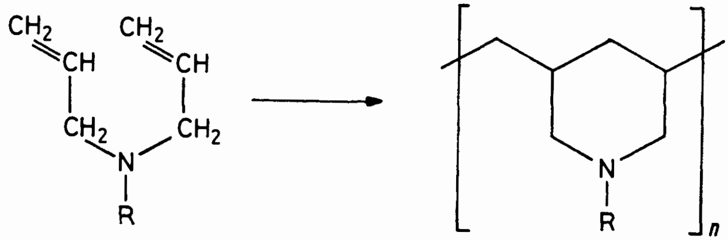
(24)



(25)

seems to be the more readily formed while the isotactic structure is the thermodynamically more stable configuration. Butler[14] has discussed other conformational aspects of the cyclopolymerization mechanism.

The parent amines, diallylamine and diallylalkylamines, of the quaternary ammonium salts concerned in the discovery of the cyclopolymerization mechanism have not been polymerized. However, derivatives with electron-withdrawing groups on the nitrogen (26) can be polymerized with radical initiators.[15] Polymerization does not occur when the electron-withdrawing group is not directly



(26) *e.g.* R = CN, CO_2Me, SO_2Ph

(27)

$(H_2C{=}CHCH_2)_2NCH_2CO_2Et$

(28)

$(H_2C{=}CHCH_2)_2NCH_2CH_2CN$

(29)

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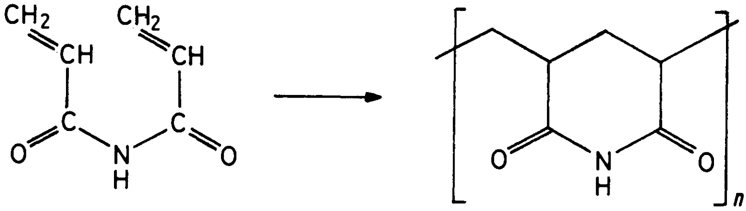
[14] G. B. Butler, *Pure Appl. Chem.*, 1962, **4**, 299.

[15] S. G. Matsoyan, G. M. Pogosyan, A. O. Dzhagalyan, and A. V. Mushegyan, *Vysokomol. Soedinenii*, 1963, **5**, 854; S. G. Matsoyan, G. M. Pogosyan, and G. A. Zhamkochyan, *Izvest. Akad. Nauk Arm. S.S.R., Khim. Nauki*, 1964, **17**, 62; V. G. Ostroverkov, L. A. Brunovskaya, and A. A. Kornienko, *Vysokomol. Soedinenii*, 1964, **6**, 925; A. Crawshaw and A. G. Jones, *Chem. and Ind.*, 1966, 2013.

joined to the nitrogen; for example, in ethyl diallylaminoacetate (28) and *N*-(2-cyanoethyl)diallylamine (29). The ability of the monomer to polymerize increases with the electron-withdrawing ability of the substituent. The solubility and fusibility of the polymers and the absence of residual unsaturation indicated that they were linear cyclopolymers. The i.r. spectra of the polymers showed absorption bands typical of the piperidine ring and the spectrum of poly(diallylacetamide) was similar to that of *N*-acetylpiperidine. *N*-substituted derivatives of dimethallylamine polymerize less readily than those of diallylamine.

Radical-initiated polymerization of diacrylamide (30)[16] yielded a soluble polymer with only a small amount of residual unsaturation. A six-membered ring (31) was presumed to be present since the polymer showed an i.r. band which corresponded with that of the carbonyl group in glutarimide.



(30) (31)

Sokolova and Rudkovskaya[17] considered the possibility of formation of both five-membered (33) and six-membered (34) ring structures by the radically initiated cyclopolymerization of dimethacrylamide and *N*-substituted dimethacrylamides (32). Bulk or solution polymerization yielded soluble, fusible polymers which contained practically no unsaturation. Polymers of similar structure but with six-membered ring units only were obtained by partial deamination of polymethacrylamides (35).

Important differences were found in the carbonyl region of the i.r. spectra of the two series of polyimides, and a comparison was made with the spectra of five- and six-membered ring cyclic imides. It was concluded that the polymerization of *N*-substituted dimethacrylamides yielded cyclopolymers containing predominantly five-membered ring repeating units. Polydimethacrylamide was the exception and contained predominantly six-membered cyclic units. Gotzen and Schroder[18] have shown that the anionic polymerization of *N*-methyldimethacrylamide yields a polymer which consists exclusively of six-membered ring units.

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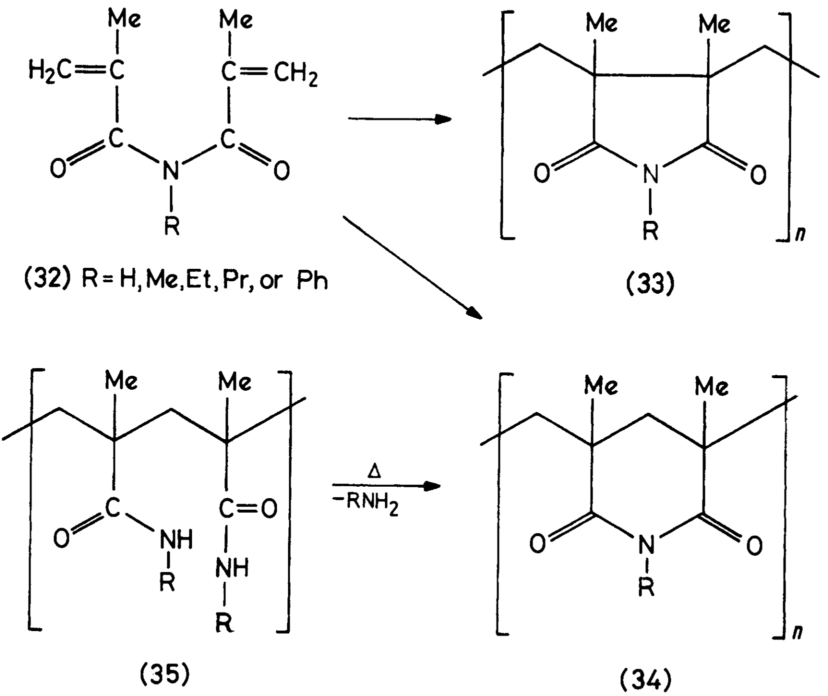
[16] T. Miyake, *Kogyo Kagaku Zasshi*, 1961, **64**, 359.

[17] T. A. Sokolova and G. D. Rudkovskaya, *J. Polymer Sci., Part C, Polymer Symposia*, 1967, **16**, 1157.

[18] F. Gotzen and G. Schroder, *Makromol. Chem.*, 1965, **88**, 133.



(32) R = H, Me, Et, Pr, or Ph

(33)

(35)

(34)

Polymers with heterocyclic repeating units containing sulphur,[19] silicon,[20] and phosphorus[21] have also been synthesized by the cyclopolymerization mechanism.

B. Large-ring Cyclopolymers.—Holt and Simpson[4] showed that intramolecular reaction was important during the formation of network polymers from diallyl esters (36) using free-radical initiators. They recognized that cyclization can

$$H_2C{=}CHCH_2O_2C{-}R{-}CO_2CH_2CH{=}CH_2$$

(36) R = O or $(CH_2)_{0-8}$

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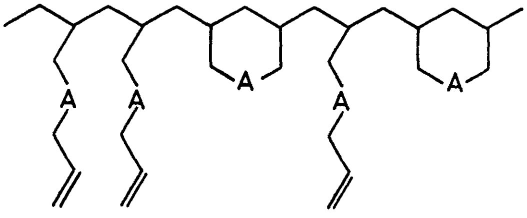
[19] S. G. Matsoyan and A. A. Saakyan, *Vysokomol. Soedinenii*, 1961, **3**, 1755; *Izvest. Akad. Nauk Arm. S.S.R., Khim. Nauki*, 1962, **15**, 463; H. Ringsdorf and C. G. Overberger, *J. Polymer Sci.*, 1962, **61**, 511; *Makromol. Chem.*, 1961, **44-46**, 418.

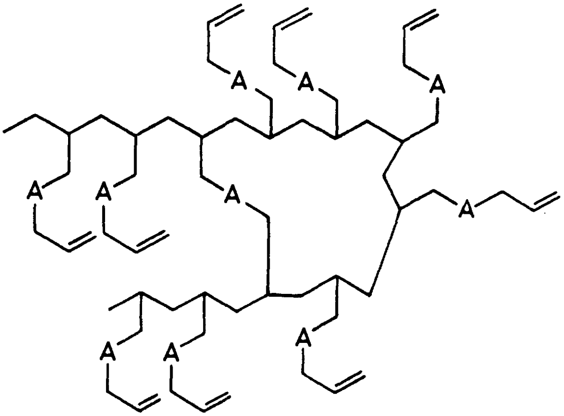
[20] V. Ya. Bagomol'nyi, *Vysokomol. Soedinenii*, 1959, **1**, 1469; G. S. Kolesnikov, S. L. Davydova, and T. N. Ermolaeva, *Vysokomol. Soedinenii*, 1959, **1**, 1493; C. S. Marvel and R. G. Woolford, *J. Org. Chem.*, 1960, **25**, 1641; G. B. Butler and R. W. Stackman, *J. Org. Chem.*, 1960, **25**, 1643; G. B. Butler and R. W. Stackman, *J. Macromol. Sci. Chem.*, 1969, **3**, 821; Hung-Chih Chang, Hang-Pao Feng, and Hsin-Te Feng, *Ko Fen Tzu T'ung Hsun*, 1964, **6**, 487; L. E. Gusel'nikov, N. S. Nametkin, L. S. Polak, and Y. I. Chernysheva, *Vysokomol. Soedinenii*, 1964, **6**, 2002; M. Furue, S. Nozakura, and S. Murahashi, *Kobunshi Kagaku*, 1967, **24**, 522; M. Sumi, S. Nozakura, and S. Murahashi, *ibid.*, p. 512.

[21] K. D. Berlin and G. B. Butler, *J. Amer. Chem. Soc.*, 1960, **82**, 2712; *J. Org. Chem.*, 1960, **25**, 2006; G. B. Butler, D. L. Skinner, W. C. Bond, and C. L. Rogers, *J. Macromol. Sci Chem.*, 1970, **4**, 1437.

occur by addition of the radical of a growing chain to a pendant allyl group in the same chain. This could be the double bond in the same monomer unit as the radical (37), or, to a lesser extent, in the penultimate or other units (38). The



(37) A = O_2CRCO_2



(38)

extent of cyclization was found to decrease with increasing separation of the allyl groups in the monomers and did not vary as a function of ring size as was known to be the case in condensation reactions. The diallyl esters of the three isomeric phthalic acids were also studied. Diallyl terephthalate exhibited a small amount of intramolecular reaction which was shown to be due to multiple cross-linking (38). Diallyl phthalate, however, was shown to be cyclized to the extent of 41%. Because a minimum of ten atoms is required for ring-closure between substituents on *para*-positions, cyclopolymerization (37) is only possible with diallyl phthalate and diallyl isophthalate.

The Ziegler-initiated polymerization of the symmetrical non-conjugated dienes $CH_2{=}CH(CH_2)_nCH{=}CH_2$, ($n$ = 2—18), has been studied.[7,22] The results show that, in all cases, soluble fractions with some cyclic recurring units are

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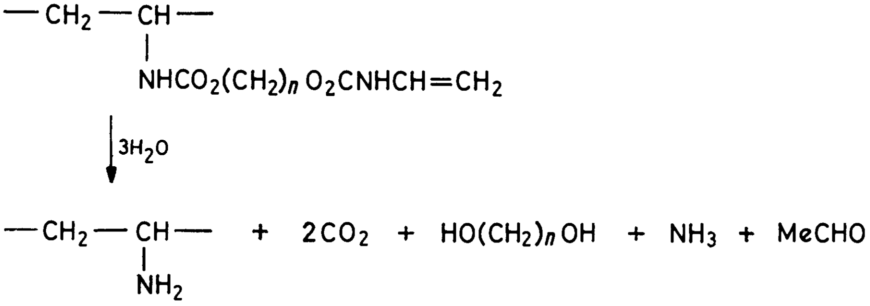
[22] C. S. Marvel and W. E. Garrison, jun., *J. Amer. Chem. Soc.*, 1959, **81**, 4737.

produced. Here the extents of cyclization correspond roughly with results which have been obtained in other cyclization reactions. Thus, the tendency to form rings is a maximum for ring sizes of five or six atoms, intermediate ring sizes form with greater difficulty (with a minimum at nine atoms), larger rings (fourteen and fifteen atoms) are easier to obtain, and the yield decreases again with still higher ring sizes.

Schulz and Stenner[23] studied the radical polymerization of a series of bis-*N*-vinyl compounds (39) and obtained completely soluble polymers at certain monomer and catalyst concentrations. The extent of cyclization at various times was calculated from the residual double-bond content of the soluble polymers. The pendant *N*-vinyl groups were determined by quantitative analysis of the acetaldehyde produced upon acidic hydrolysis of the polymers (40). At the beginning of the polymerization the polymers contain about 83% cyclization which is relatively independent of the number of atoms in the ring. The polymerization of the bis-*N*-vinyl compounds (41) was also studied. The vinyl groups

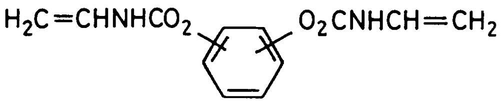
$$H_2C{=}CHNHCO_2(CH_2)_nO_2CNHCH{=}CH_2$$

(39) n = 2,4,6, or 8



$$-CH_2-\underset{\displaystyle NHCO_2(CH_2)_nO_2CNHCH{=}CH_2}{\underset{|}{CH}}- \xrightarrow{3H_2O} -CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}- + 2CO_2 + HO(CH_2)_nOH + NH_3 + MeCHO$$

(40)



(41) o, m, or p

of the hydroquinone derivative polymerized almost independently and eventually cross-linking occurred. However, the catechol derivative, under the same condi-

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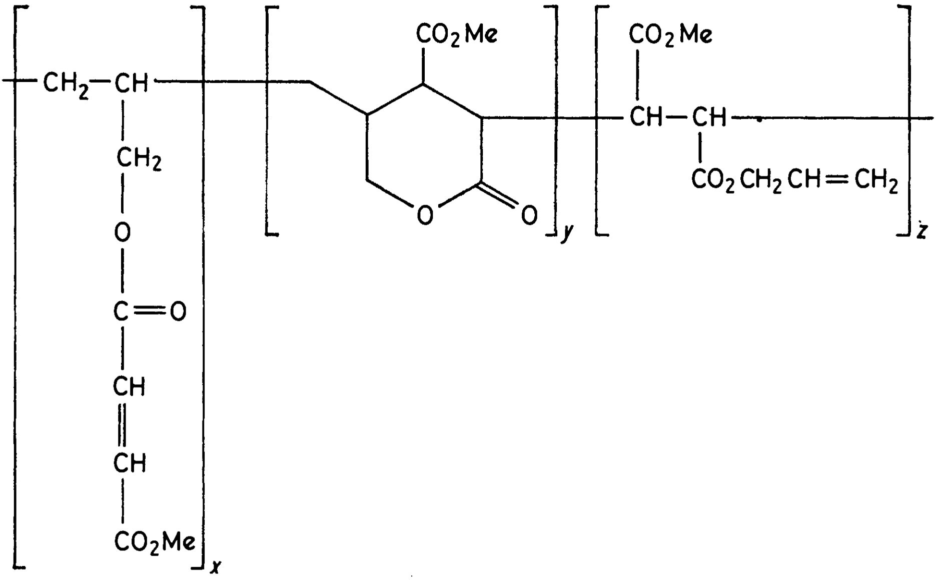
[23] R. C. Schulz and R. Stenner, *Makromol. Chem.*, 1966, **91**, 10.

tions, gave a soluble polymer with approximately 70% cyclization. These results agree qualitatively with those of Holt and Simpson on the allyl esters of the three isomeric phthalic acids.

C. Polymerization of Unsymmetrical Monomers.—Barnett, Crawshaw, and Butler[24] studied the free-radical polymerization, in bulk, of unsaturated esters of maleic and fumaric acids, and found that the polymerization of such unsymmetrical non-conjugated dienes, where the double bonds are of different reactivity, resulted in some cyclopolymerization. Although cross-linked polymers were eventually formed, when the polymerization was stopped just before the gel point a series of soluble polymers containing a considerable amount of cyclization (23—63%) were obtained. The highest degrees of cyclization were obtained from monomers having double bonds of comparable reactivity toward copolymerization but with little tendency to homopolymerize. Structure (42) was proposed for poly(allyl methyl fumarate) where $x : y : z = 1 : 3 : 1$. It has been shown[24,25] that polymers obtained from allyl esters of maleic acid contain both five- and six-membered ring structures. Trossarelli, Guaita, and Priola[26]



(42)

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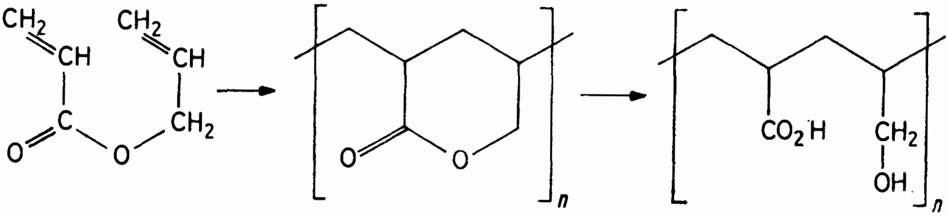
[24] M. D. Barnett, A. Crawshaw, and G. B. Butler, *J. Amer. Chem. Soc.*, 1959, **81**, 5946.

[25] I. A. Arbuzova, E. F. Fedorova, S. A. Plotkina, and R. M. Minkova, *Vysokomol. Soedinenii* (*A*), 1967, **9**, 189.

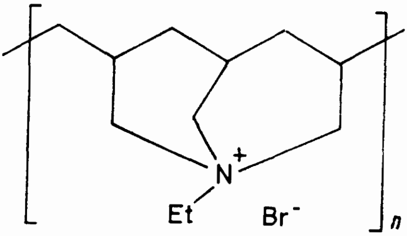
[26] L. Trossarelli, M. Guaita, and A. Priola, *Ricerca Sci.*, 1965, **35**(II-A), 379, 429; *Makromol. Chem.*, 1967, **100**, 174; *Ann. Chim.* (*Italy*), 1966, **56**, 1065; *Ricerca Sci.*, 1966, **36**, 993; *Polymer*, 1968, **9**, 233; *J. Polymer Sci., Part. C, Polymer Symposia*, 1969, **16**, 4713.

have shown that allyl acrylate, allyl methacrylate, *N*-allylacrylamide, *N*-allylmethacrylamide, and vinyl crotonate all yield soluble polymers, under suitable conditions, which contain appreciable amounts of cyclic units. Polymerization in dilute solution and to a low conversion was necessary in order to obtain these soluble polymers. Schulz *et al.*[27] have obtained a 1 : 1 copolymer of allyl alcohol and acrylic acid by hydrolysis of the cyclopolymer obtained from allyl acrylate (43); the copolymerization parameters show that a copolymer of this type cannot be obtained directly from the monomers.

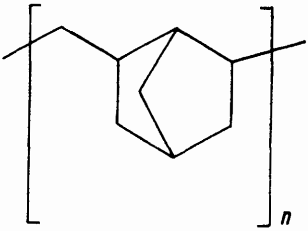


(43)

D. Polycyclic Structures.—Bicyclic and tricyclic structures can be formed by a succession of ring-closures within a single monomer molecule before propagation to another molecule occurs. Trifan and Hoglen[28] obtained soluble polymers,



(44)



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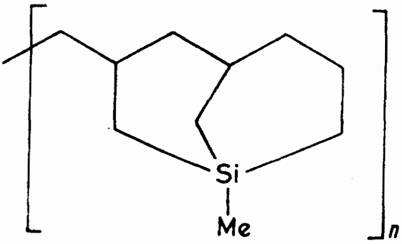

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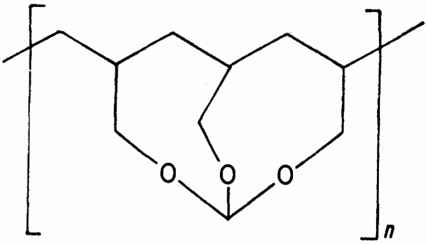

(47)

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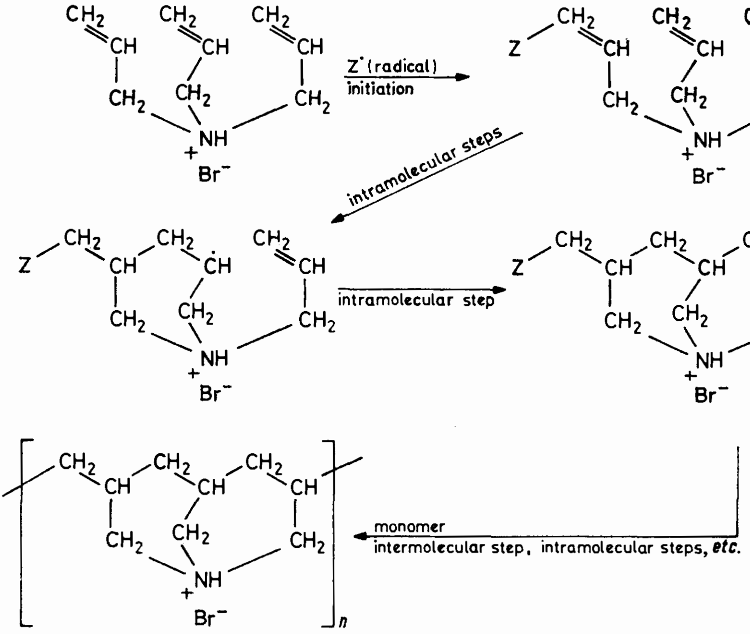
[27] R. C. Schulz, M. Marx, and H. Hartmann, *Makromol. Chem.*, 1961, **44-46**, 281.
[28] D. S. Trifan and J. J. Hoglen, *J. Amer. Chem. Soc.*, 1961, **83**, 2021.

having little residual unsaturation, from triallylethylammonium bromide, 3-vinylhexa-1,5-diene, triallylmethylsilane, and triallylorthoformate and proposed structures (44)—(47) respectively, for their repeating units. Maysoyan *et al.*[29] have also established that polymers containing bicyclic units can be obtained *via* a cyclopolymerization mechanism (Scheme 2). Interestingly, tetra-allylammonium bromide polymerizes[28] with three intramolecular reactions before the intermolecular step, to give a linear polymer containing tricyclic repeating units.



Scheme 2

Soluble polymers, shown by spectroscopic analysis, to contain nortricyclene repeating units, have been obtained by the transannular polymerization of bicyclo[2,2,1]hepta-2,5-diene and derivatives[30] [(48)—(50)]. *cis,cis*-Cyclo-octa-

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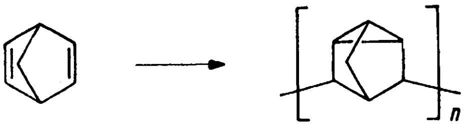
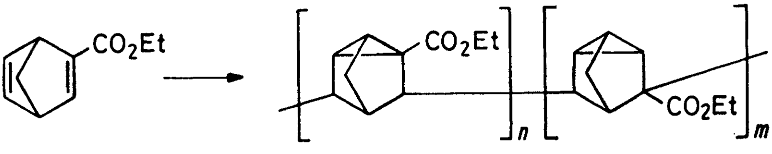
[29] S. G. Matsoyan, G. M. Pogosyan, and M. A. Eliazyan, *Vysokomol. Soedinenii*, 1963, **5**, 777.

[30] P. J. Graham, E. L. Buhle, and N. Pappas, *J. Org. Chem.*, 1961, **26**, 4658; R. H. Wiley, W. H. Rivera, T. H. Crawford, and N. F. Bray, *J. Polymer Sci.*, 1962, **61**, S38; G. Sartori, A. Valvassori, V. Turba, and M. P. Lachi, *Chimica e Industria*, 1963, **45**, 1529; J. P. Kennedy and J. A. Hinlicky, *Polymer*, 1965, **6**, 133; J. P. Kennedy and H. S. Makowski, *J. Polymer Sci., Part C, Polymer Symposia*, 1968, **22**, 247.



(48)



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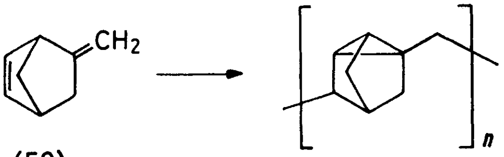
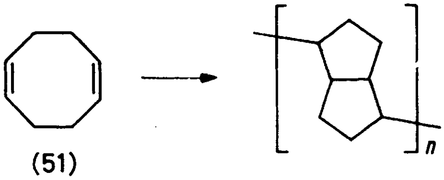


(50)

1,5-diene[31] (51) and its 1-methyl derivative[32] (52) have yielded soluble polymers for which bicyclo[3,3,0]octane repeating units are suggested on the basis of their i.r. spectra. Polymers containing bicyclic units have also been obtained by the polymerization of 1,4-dimethylenecyclohexane (53),[33] 1-methylene-4-vinyl-



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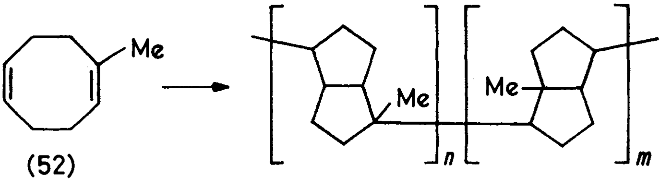

(52)

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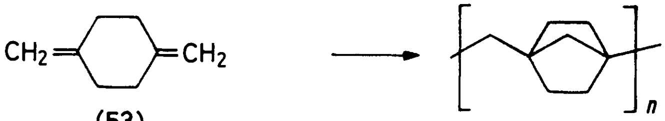
[31] B. Reichel, C. S. Marvel, and R. Z. Greenley, *J. Polymer Sci., Part A*, 1963, **1**, 2935.

[32] A. Valvassori, G. Sartori, V. Turba, and M. P. Lachi, *J. Polymer Sci., Part C, Polymer Symposia*, 1967, **16**, 23.

[33] L. E. Ball and H. J. Harwood, *Polymer Preprints*, 1961, **2**, 59.

cyclohexane (54),[34] 4-vinylcyclohexene (55),[35] and 1-allyl-2-methylenecyclohexane (56).[36]



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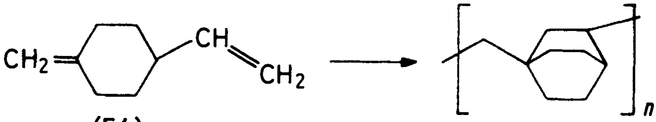

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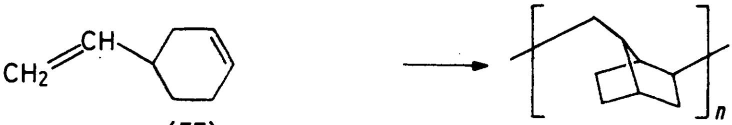

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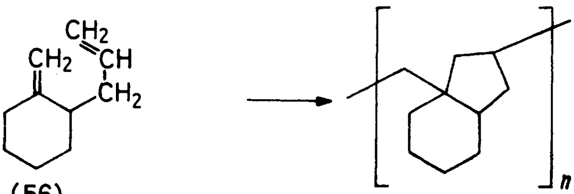
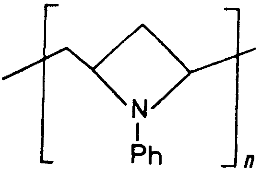


(56)

The examples of cyclopolymerization already discussed have been such that the cyclic structures were derived from a single molecule of a monomer. Chang and Price[37] found that free-radical polymerization of *NN*-divinylaniline, as a solution in benzene, yielded a soluble polymer having a negligible amount of



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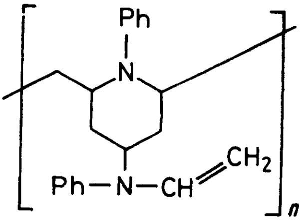

(58)

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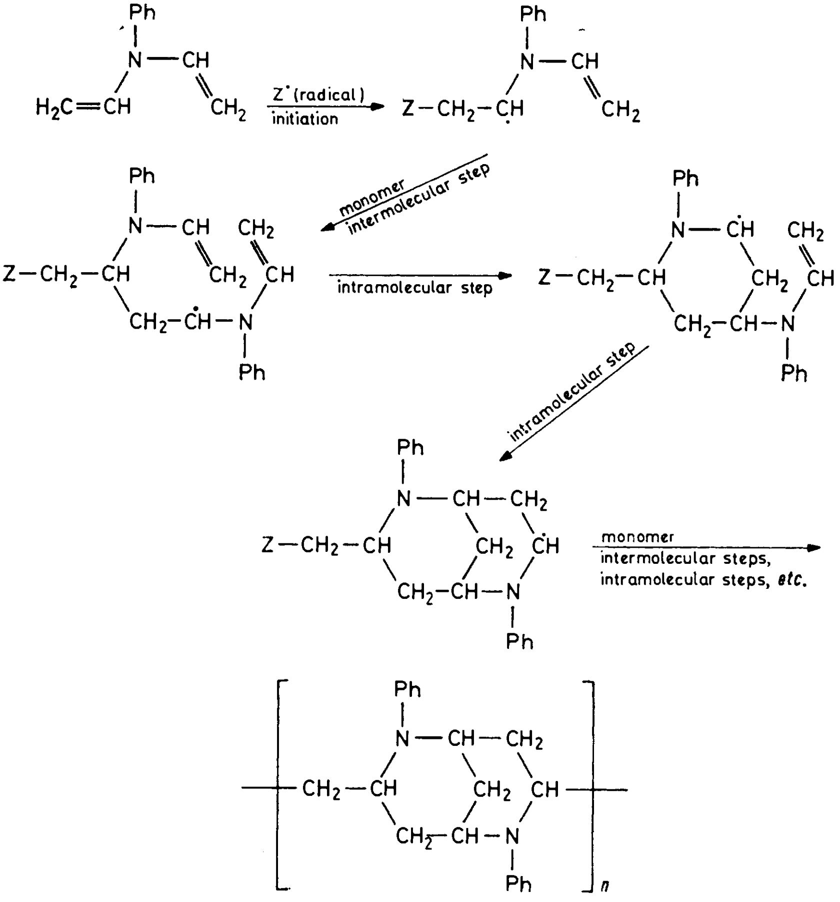
[34] G. B. Butler, M. L. Miles, and W. S. Brey, jun., *J. Polymer Sci., Part A*, 1965, **3**, 723.
[35] G. B. Butler and M. L. Miles, *J. Polymer Sci., Part A*, 1965, **3**, 1609.
[36] G. B. Butler and M. L. Miles, *Polymer Eng. Sci.*, 1966, **6**, 1.
[37] E. Y. C. Chang and C. C. Price, *J. Amer. Chem. Soc.*, 1961, **83**, 4650.

residual unsaturation. A spectroscopic study of the polymer ruled out the presence of a four-membered ring-structure (57) and supported their proposal that a bicyclic unit had formed as a result of the cyclization of two *NN*-divinylaniline molecules (Scheme 3). Bulk polymerization led to a soluble polymer



Scheme 3

having about 50% residual unsaturation, for which structure (58) was proposed.

Soluble polymers containing approximately 20% residual unsaturation have been obtained[38,39] by radical homopolymerization of divinyl ether. Structures (59)—(62) are postulated as the main units in the polymers and kinetic evidence

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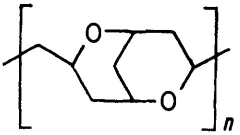
[38] C. Aso and S. Ushio, *Kogyo Kagaku Zasshi*, 1962, **65**, 2085; C. Aso, S. Ushio, and M. Sogabe, *Makromol. Chem.*, 1967, **100**, 100.

[39] M. Guaita, G. Camino, and L. Trossarelli, *Makromol. Chem.*, 1969, **130**, 243; 252; 1970, **131**, 237.



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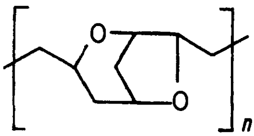
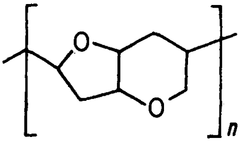


(60)



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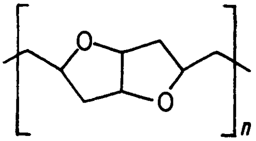
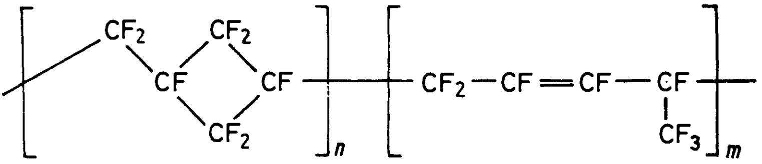


(62)

is given that both five- and six-membered rings are formed in the cyclization steps.

Perfluoropenta-1,4-diene has been polymerized[40] by γ-irradiation at 100—170 °C under 8000—15 000 atmospheres pressure. Some isomerization to perfluoropenta-1,3-diene occurred with subsequent copolymerization of the mixture. Structure (63) was proposed for the polymers but evidence of the presence of a four-membered ring was not provided. Cyclopolymerization of penta-1,4-diene[41] and some substituted divinyl ketones[42,43] has been reported.



(63) $n>m$

3 Cyclopolymerization involving Other Groups

Compounds with other polymerizable groups in 1,5- or 1,6-positions (diynes, diepoxides, dialdehydes, di-isocyanates, and dinitriles) have been shown to undergo cyclopolymerization.

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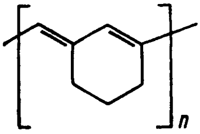
[40] D. W. Brown, J. E. Fearn, and R. E. Lowry, *J. Polymer Sci., Part A*, 1965, **3**, 1641; J. E. Fearn, D. W. Brown, and L. A. Wall, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1966, **4**, 131.

[41] D. S. Trifan, R. A. Shelden, and J. J. Hoglen, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1968, **6**, 1605.

[42] M. G. Avetyan, E. G. Darbinyan, A. A. Saakyan, F. S. Kinoyan, and S. G. Matsoyan, *Vysokomol. Soedinenii*, 1964, **6**, 13; S. G. Matsoyan, M. G. Avetyan, and E. G. Darbinyan, *Izvest. Akad. Nauk Arm. S.S.R., Khim. Nauki*, 1964, **17**, 412.

[43] I. A. Arbuzova and I. K. Mosevich, *Vysokomol. Soedinenii*, 1964, **6**, 13.

Stille and Frey[44] prepared soluble polymers from hepta-1,6-diyne using Ziegler catalysts, and proposed the structure (64) in which the main chain is a conjugated system of double bonds. However, a polycyclotrimer structure (65) for this polymer is favoured by Hubert and Dale.[45] Polymerization of propynoic anhydride[46] using KCNS, KCN, KCl, KBr, or KI as catalyst yielded a black powder, having a metallic gloss, for which structure (66) was proposed.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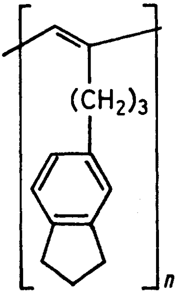

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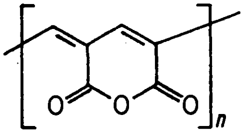
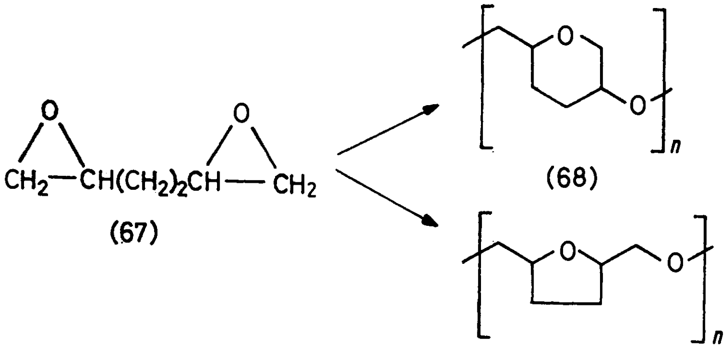

(66)

1,2,5,6-Diepoxyhexane (67) polymerizes, using a variety of initiators, to linear cyclopolymers, and repeating units containing tetrahydropyran (68) and tetrahydrofuran (69) rings have been suggested by different authors.[47]



(67)

(68)

(69)

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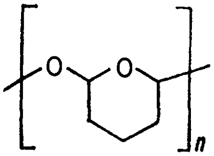
[44] J. K. Stille and D. A. Frey, *J. Amer. Chem. Soc.*, 1961, **83**, 1697.

[45] A. J. Hubert and J. Dale, *J. Chem. Soc.*, 1965, 3160.

[46] R. I. Yakhimovich, E. A. Shilov, and G. F. Dvorko, *Doklady Akad. Nauk S.S.S.R.*, 1966, **166**, 388.

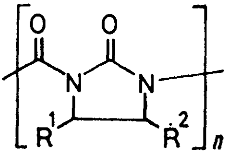
[47] J. K. Stille and B. M. Culbertson, *J. Polymer Sci., Part A*, 1964, **2**, 405; C. Aso and Y. Aito, *Makromol. Chem.*, 1964, **73**, 141; R. S. Bauer, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1967, **5**, 2192.

It was reported[48] in 1908 that glutaraldehyde yielded a soluble, solid material on standing at room temperature, but no structure was suggested for the product. After the discovery of cyclopolymerization, the spontaneous and cationic polymerization of glutaraldehyde was investigated[49] and gave the expected results. Soluble, thermally unstable, cyclopolymers were readily obtained for which a six-membered ring structure (70) was proposed. A number of other dialdehydes, including succinaldehyde,[50] adipaldehyde,[51] malealdehyde,[52] and *o*-phthalaldehyde,[53] have been similarly shown to undergo cyclopolymerization.



(70)

King[54] reported the cyclopolymerization of several aliphatic 1,2-di-isocyanates at low temperature using sodium cyanide in DMF as catalyst. Soluble high molecular weight products were obtained for which, from the evidence, structures (71) were given. Iwakura *et al.*[55] studied the cyclopolymerization of $\alpha\omega$-polymethylene di-isocyanates (72; n = 1—4) and indicated that two different structural units, (73) and (74), are possible depending on whether the poly-



(71)

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[48] C. Harries and L. Tank, *Ber.*, 1908, **41**, 1701.

[49] C. Aso and Y. Aito, *Makromol. Chem.*, 1962, **58**, 195; K. Meyersen, R. C. Schulz, and W. Kern, *Makromol. Chem.*, 1962, **58**, 204; C. G. Overberger, S. Ishida, and H. Ringsdorf, *J. Polymer Sci.*, 1962, **62**, S1.

[50] C Aso, A. Furuta, and Y. Aito. *Makromol. Chem.*, 1965, **84**, 126; Y. Aito, T. Matsuo, and C. Aso, *Bull. Chem. Soc. Japan*, 1967, **40**, 130.

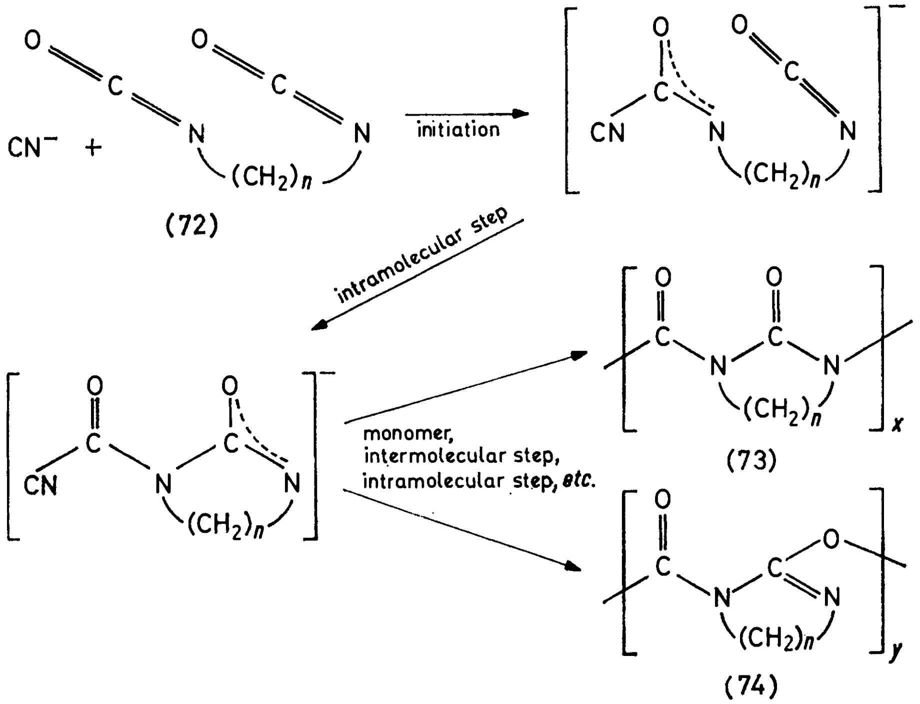
[51] C. Aso and Y. Aito, *Kobunshi Kagaku*, 1966, **23**, 564.

[52] C. Aso, T. Kunitake, M. Miura, and K. Koyama, *Makromol. Chem.*, 1968, **117**, 153.

[53] C. Aso and S. Tagami, *J. Polymer Sci, Part B, Polymer Letters*, 1967, **5**, 217; C. Aso, S. Tagami and T. Kunitake, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1969, **7**, 497; C. Aso and S. Tagami, *Macromolecules*, 1969, **2**, 414.

[54] C. King, *J. Amer. Chem. Soc.*, 1964, **86**, 437.

[55] Y. Iwakura, K. Uno, and K. Ichikawa, *J. Polymer Sci., Part A*, 1964, **2**, 3387.



Scheme 4

merization proceeds through the N=C or C=O bonds of the second isocyanato-group (Scheme 4). The proportion of (74) units in the polymers was estimated by a quantitative aminolysis using di-n-butylamine. 1,2-Di-isocyanatoethane (72; $n = 2$) yielded a cyclopolymer consisting entirely of units of structure (74). It has been observed that an isocyanato-group on a secondary carbon atom does not polymerize using sodium cyanide in DMF as catalyst: for example, 2-isocyanatopropane,[56] isocyanatocyclohexane,[56] and *trans*-1,3-di-isocyanatocyclohexane,[57] in which the axial–equatorial arrangement of the isocyanato-groups does not allow the formation of a cyclopolymer. However, 1,2-di-isocyanatocyclohexane,[54] *cis*-1,3-di-isocyanatocyclohexane,[57] and *cis*- and *trans*-1,3,5-tri-isocyanatocyclohexane[58] all readily cyclopolymerized. It appears that formation of a five- or six-membered ring is a driving force for polymerization of an otherwise poorly polymerizable structure.

Liepins *et al.*[59] have prepared homopolymers and copolymers of fumaronit-

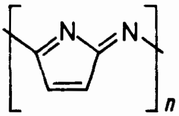
[56] V. E. Shashoua, W. Sweeney, and R. F. Tietz, *J. Amer. Chem. Soc.*, 1960, **82**, 866.

[57] G. C. Corfield and A. Crawshaw, *J. Macromol. Sci. Chem.*, 1971, **5**, 3.

[58] G. B. Butler and G. C. Corfield, *J. Macromol. Sci. Chem.*, 1971, **5**, 37.

[59] R. Liepins, D. Campbell, and C. Walker, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1968, **6**, 3059; R. Liepins, *Makromol. Chem.*, 1968, **118**, 36.

rile, maleonitrile, succinonitrile, diphenylmaleonitrile, and diphenylsuccinonitrile using free-radical initiators at high temperatures. Black, infusible, but soluble polymers were obtained for which the completely conjugated structures (75)—(78) were proposed.



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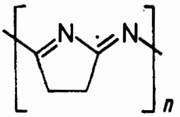

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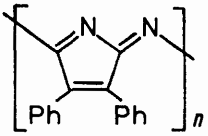

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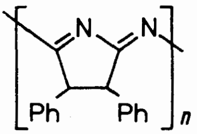
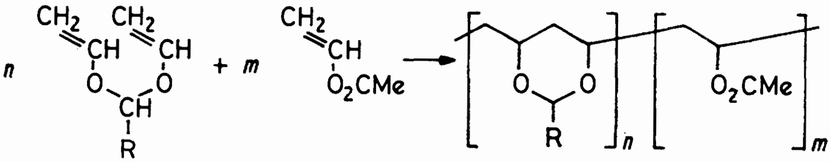


(78)

4 Cyclocopolymerization

Many examples of the copolymerization of 1,6-dienes with vinyl monomers and other co-monomers such as sulphur dioxide can be found in the literature. In almost every case the predominant role of the diene was cyclization and cross-linked products were not formed. Matsoyan *et al.*[60] have shown that the radical copolymerization of divinyl acetals with vinyl acetate yields soluble, completely saturated products. It was found, whatever the molar proportions of the components and whatever the degree of reaction, that the composition of the copolymer formed was identical with the initial mixture (79). Harada *et al.*[61] have



(79)

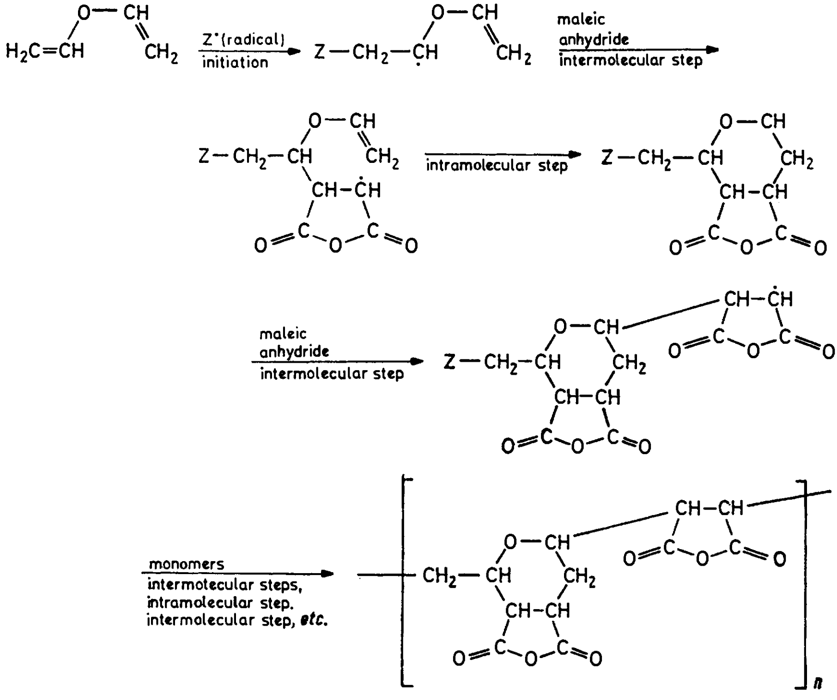
[60] S. G. Matsoyan, M. G. Avetyan, and M. G. Voskanyan, *Vysokomol. Soedinenii*, 1962, **4**, 882; S. G. Matsoyan, M. G. Voskanyan, E. Ts. Gevorkyan, and A. A. Cholakyan, *Izvest. Akad. Nauk Arm. S.S.R., Khim. Nauki*, 1964, **17**, 420.

[61] S. Harada and M. Katayama, *Makromol. Chem.*, 1966, **90**, 177; S. Harada and K. Arai, *Makromol. Chem.*, 1967, **104**, 64, **107**, 78.

obtained soluble, saturated products by the radical copolymerization of diallyl quaternary ammonium salts with sulphur dioxide, in which the co-monomers are incorporated in the ratio 1 : 1, irrespective of the molar ratio in the monomer mixture.

Butler and co-workers[62] have shown that 1,4-dienes are capable of copolymerizing to give a cyclic repeating unit containing both monomers. The cyclocopolymerization of divinyl ether and maleic anhydride illustrates the reaction (Scheme 5). A variety of 1,4-dienes and alkene comonomers have been studied[62,37].

Meyersen and Wang[63] have described the cyclocopolymerization of some 1,5- and 1,6-bicyclic dienes with maleic anhydride. Soluble, low molecular



Scheme 5

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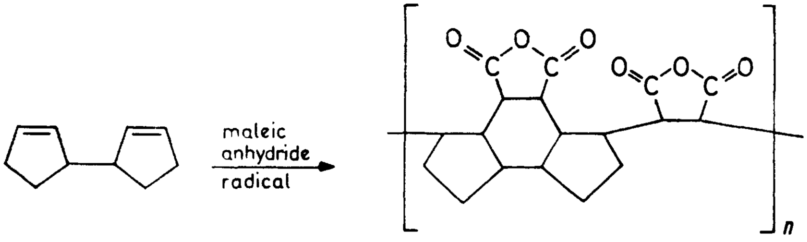
[62] J. M. Barton, G. B. Butler, and E. C. Chapin, *J. Polymer Sci., Part A*, 1965, **3**, 501; G. B. Butler and R. B. Kasat, *ibid.*, p. 4205; G. B. Butler, G. Vanhaeren, and M. F. Ramadier, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1967, **5**, 1265; G. B. Butler and K. C. Joyce, *J. Polymer Sci., Part C, Polymer Symposia*, 1968, **22**, 45; G. B. Butler and A. F. Campus, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1970, **8**, 523, 545; G. B. Butler, *J. Macromol. Sci. Chem.*, 1971, **5**, 219.

[63] K. Meyersen and J. Y. C. Wang, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1967, **5**, 1845.

weight, 2 : 1 copolymers were obtained for which fused ring structures (80) were proposed as the main repeating units (80). The cyclocopolymerization of 1,5-dienes and sulphur dioxide has also been studied[64] and cyclic repeating units suggested for the copolymers obtained from hexa-1,5-diene (81), *cis,cis*-cycloocta-1,5-diene and some bicyclic dienes.



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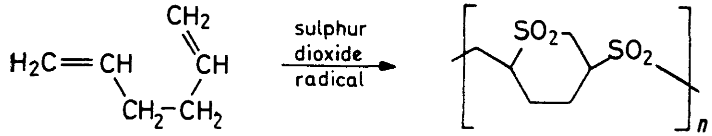

(81)

5 Kinetics and Mechanism of Cyclopolymerization

Two features of cyclopolymerization which characterize it are: firstly, where symmetrical bifunctional monomers can form five- or six-membered rings, the intramolecular propagation reaction predominates, almost exclusively, over the intermolecular reaction such that soluble, essentially saturated, linear polymers are obtained; and, secondly, the reactivity of bifunctional monomers which produce such cyclopolymers is greater than that of monofunctional monomers of similar structure.

Kinetic studies have attempted to define the rate and energy factors which control the cyclopolymerization. The process of free-radical cyclopolymerization of a symmetrical bifunctional monomer may be described by the following reactions:

$$\begin{array}{lrll} \text{initiation} & \mathrm{I} & \xrightarrow{k_d} \mathrm{2I\cdot} & \\ & \mathrm{I\cdot} + \mathrm{M} & \xrightarrow{k_i} \mathrm{M_1\cdot} & \\ \text{propagation} & \mathrm{M_1\cdot} & \xrightarrow{k_c} \mathrm{M_c\cdot} & \text{(intramolecular)} \end{array}$$

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[64] J. K. Stille and D. W. Thomson, *J. Polymer Sci.*, 1962, **62**, S118; A. H. Frazer and W. P. O'Neill, *J. Amer. Chem. Soc.*, 1963, **85**, 2613; A. H. Frazer, *J. Polymer Sci., Part A*, 1964, **2**, 4031; K. Meyersen and J. Y. C. Wang, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1967, **5**, 1827; T. Yamaguchi and T. Ono, *Chem. and Ind.*, 1968, 769.

$$\begin{array}{lll} & \mathrm{M_1}\cdot + \mathrm{M} \xrightarrow{k_1} \mathrm{M_1}\cdot & \text{(intermolecular)} \\ & \mathrm{M_C}\cdot + \mathrm{M} \xrightarrow{k_{c1}} \mathrm{M_1}\cdot & \text{(intermolecular)} \\ \text{termination} & \mathrm{M_1}\cdot + \mathrm{M_1}\cdot \xrightarrow{k_{11}} \text{product} & \\ & \mathrm{M_C}\cdot + \mathrm{M_C}\cdot \xrightarrow{k_{22}} \text{product} & \\ & \mathrm{M_1}\cdot + \mathrm{M_C}\cdot \xrightarrow{k_{12}} \text{product} & \end{array}$$

Expressions have been developed giving the rate of loss of double bonds in terms of the initial monomer and initiator concentrations and associated rate constants.[5,65–68] Most expressions predict that the rate of polymerization will be proportional to $[\mathrm{M}][\mathrm{I}]^{\frac{1}{2}}$. Results of experimental investigations are given in Table 1. Smets and co-workers[13,65] attributed the diversity of the results obtained to increases in viscosity of the solution as polymerization proceeds, the progressive heterogeneity of the reaction medium, and the trapping of radicals, rather than to failure of the proposed kinetics. Other workers[66,67] have derived alternative rate expressions.

Table 1 *Dependence of rate of cyclopolymerization on monomer and initiator concentration*

Monomer[a]	*Solvent*	*Order of reaction, with respect to*	
		[M]	[I]
Methacrylic anhydride	DMF	1.5	0.5
Methacrylic anhydride	cyclohexanone	1.0	0.58; 0.66
Methacrylic anhydride	DMF	1.0	0.60
Acrylic anhydride	cyclohexanone	complex	0.65—1.0
Divinyl formal	benzene	1.5—2.0	0.75
Diallylcyanamide	benzene	1.0	1.0
Diallylcyanamide	*m*-cresol	2.0	1.0
Dicyanoheptadiene	DMF	1.0	0.5

[a] Initiator in all cases is αα′-azobisisobutyronitrile

Accurate determinations of the residual unsaturation as a function of monomer concentration and temperature have been made for a number of cyclopolymers.[5,8,65,66,68,69] From the data the ratio of rate constants and the difference in energy for intramolecular and intermolecular reaction may be obtained

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[65] G. Smets, P. Hous and N. Deval, *J. Polymer Sci., Part A*, 1964, **2**, 4825.

[66] Y. Minoura and M. Mitoh, *J. Polymer Sci., Part A*, 1965, **3**, 2149.

[67] K. Uno, K. Tsuruoka, and Y. Iwakura, *J. Polymer Sci., Part A-1, Polymer Chem*, 1968, **6**, 85.

[68] G. B. Butler and S. Kimura, *J. Macromol. Sci. Chem.*, 1971, **5**, 181.

[69] T. F. Gray, jun., Ph.D. Thesis, University of Florida, 1964.

(Table 2). The equation[70] which relates the experimentally determined fraction of cyclic units (f_c) to monomer concentration is:

$$\frac{1}{f_c} = 1 + 2\frac{k_i}{k_c}[\mathrm{M}]$$

Table 2 *Ratio of rate constants and differences in activation energy between intramolecular and intermolecular propagation*

Monomer	*Solvent*	$k_c : k_i$/mol l^{-1}	$(E_c - E_i)$/ kcal mol^{-1}
Methacrylic anhydride	DMF	2.4	2.6
Methacrylic anhydride	DMF	4.0—5.5	—
Methacrylic anhydride	cyclohexanone	45	—
Acrylic anhydride	cyclohexanone	5.9	2.4
Acrylic anhydride	toluene	11.1	2.3
Divinyl formal	benzene	130	2.6
Dicyanoheptadiene	DMF	143	—
o-Divinylbenzene	benzene	2.1—4.0	1.9

The difference in energy ($E_c - E_i$) can be calculated from the slope of a plot of $\log\left(\frac{1}{f_c} - 1\right)$ *versus* $\frac{1000}{T}$ for a constant monomer concentration.

In order for the kinetic equations to be valid, the monomer concentration must be assumed to be the same before and after polymerization and any unit which fails to cyclize must not enter another polymer chain. It is also assumed that the degrees of polymerization are high enough such that the differences in possible termination steps are negligible. Generally, conversions of 0—3% are experimentally satisfactory. The results indicate that intramolecular propagation requires greater activation energy than the intermolecular reaction, but that the rate of cyclization is considerably larger than that for intermolecular propagation.

As a fundamental explanation of cyclopolymerization Butler proposed[71] that an electronic interaction occurs between the unconjugated double bonds of 1,6-dienes (82), or between the intramolecular double bond and the reactive species after initiation (83). Such interactions would be expected to provide an energetically favourable pathway from monomer to cyclic product.

Butler and co-workers[68,72–78] have investigated the mechanism of cyclo-

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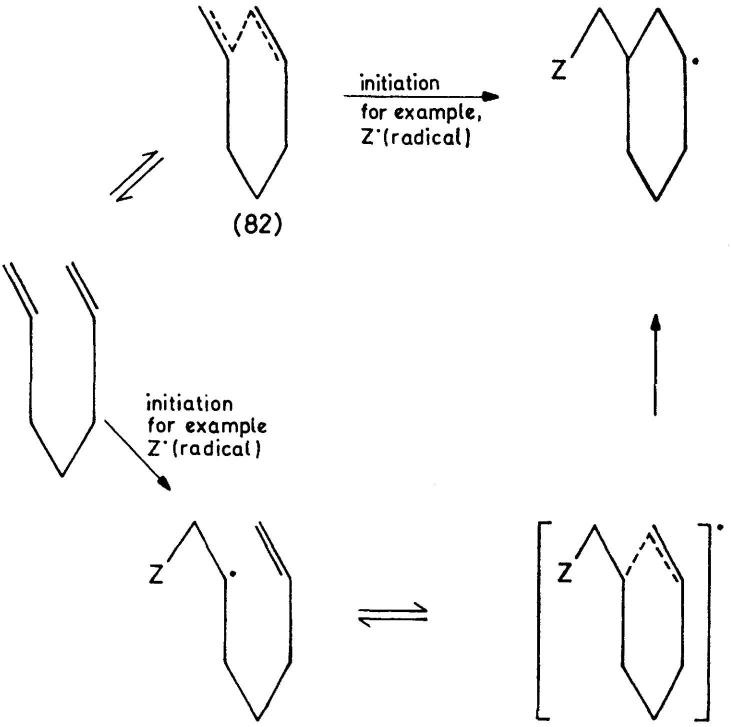
[70] J. Mercier and G. Smets, *J. Polymer Sci., Part A*, 1963, **1**, 1491.
[71] G. B. Butler, *J. Polymer Sci.*, 1960, **48**, 279.
[72] G. B. Butler and M. A. Raymond, *J. Polymer Sci., Part A*, 1965, **3**, 3413.
[73] G. B. Butler and T. W. Brooks, *J. Org. Chem.*, 1963, **28**, 2699.
[74] G. B. Butler and M. A. Raymond, *J. Org. Chem.*, 1965, **30**, 2410.
[75] G. B. Butler and B. Iachia, *J. Macromol. Sci. Chem.*, 1969, **3**, 803.
[76] G. B. Butler and W. L. Miller, *J. Macromol. Sci. Chem.*, 1969, **3**, 1493.
[77] G. B. Butler and G. R. Myers, *J. Macromol. Sci Chem.*, 1971, **5**, 105.
[78] G. B. Butler and G. R. Myers, *J. Macromol. Sci. Chem.*, 1971, **5**, 135.



(82)

(83)

polymerization in detail and have presented spectroscopic and kinetic evidence in support of an intramolecular electronic interaction. However, until a satisfactory explanation can be offered for the observed difference in activation energies (that is $E_c > E_i$), the use of electronic interaction as the sole explanation of the preference for cyclization is not justified.

Gibbs and Barton[5] consider steric effects to be important in the cyclopolymerization mechanism. The rate of intermolecular reaction of an initiated monomer molecule would be expected to be lower than that of a monofunctional monomer of similar structure but with less than five atoms in the pendant group. The presence of the large pendant group would tend to prevent intermolecular reaction from occurring at a rate that might be expected simply on the basis of the activation energy for the step. Further, the pendant double bond will frequently be presented to the reactive centre in a conformation which is favourable for reaction. However, a mechanism advocating complete steric control of cyclopolymerization would require $E_c - E_i$ to be zero, since the double bonds are considered to be identical and the intramolecular and intermolecular activation energies would be the same. Such a mechanism is not consistent with the fact that $E_c - E_i$ is, experimentally, greater than zero.

Butler and co-workers[62,79] have investigated the kinetics and mechanism of cyclocopolymerization. They interpret their results as consistent with participation of charge-transfer complexes in the process.

6 Conclusion

Since Butler and Angelo reported the cyclopolymerization of diallyl quaternary ammonium salts in 1957,[1] it has been shown that intramolecular–intermolecular polymerization can occur in a wide variety of bifunctional monomers. Although the literature dealing with cyclopolymerization shows that research in this field has generally been approached in a synthetic manner, the precise structure of the cyclopolymers has been elucidated in only a few cases and the correlation with telomerization reactions is unsatisfactory.[80] A comparative study of the products of the telomerization and cyclopolymerization of bifunctional monomers should provide valuable information on the mechanism. A significant amount of material on the kinetics and driving force of the reaction has already appeared but interpretation of the work in these areas is difficult because the results are neither conclusive nor in complete agreement with each other.

The author is grateful to Dr. Allan Crawshaw for helpful criticism in the preparation of this review.

[79] G. B. Butler, *Pure Appl. Chem.*, 1970, **23**, 255.

[80] C. Aso, *Pure Appl. Chem.*, 1970, **23**, 287; N. O. Brace, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1970, **8**, 2091; E. De Witte and E. J. Goethals, *J. Macromol. Sci. Chem.*, 1971, **5**, 73.