Determination of the Composition of Cyclopolymers in Terms of Structural Units

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Determination of the Composition of Cyclopolymers in Terms of Structural Units*

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SUMMARY

A method based on the analytical evaluation of residual unsaturations and on the knowledge of the cyclization ratios is presented for the determination of the cyclopolymer composition in terms of structural units. The application of this method to the products of the free radical polymerization of vinyl-trans-crotonate and of divinyl ether is described.

INTRODUCTION

Any attempt to interpret the cyclopolymerization of unconjugated dienes on a rational basis, and particularly to find the reasons why intramolecular chain propagation is so often favored over the intermolecular one, must necessarily rest upon as detailed a knowledge as possible of the structure of the polymers formed in this process. Unfortunately, the direct analytical determination of the different structural units in a cyclopolymer is frequently a very difficult task. Actually, owing to the fact that the cyclic units usually lack any peculiarity from an analytical point of view,

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it is seldom possible to have more information than that derived from the
evaluation of the mole fraction f_U of the monomer molecules which have
introduced only one of their unsaturations into the polymer chain, the
other one remaining as a pendant group. This is obviously accomplished
through the determination of the residual unsaturation content in the
cyclopolymer; the mole fraction f_S of the monomer molecules which have
contributed to the polymer chain growth with both their unsaturations,
and are assumed to have led to cyclic structural units, is then given by
$1 - f_U$.

This procedure might be satisfactory for characterizing those cyclo-
polymers in which only one kind of cyclic structural units is present, but
must be considered as inadequate when different cyclic units can have
been formed during the polymer chain growth. This is the case, for in-
stance, of the cyclopolymers obtained from an unsymmetrical diene of
general formula $A_1 = A_2 - - - - B_2 = B_1$ ($A_1 = A_2 -$ and $B_1 = B_2 -$
being two different olefinic groups, and the dashed line representing a
chain of two or more divalent atoms or groups). Depending on whether
$A_1 = A_2 -$ or $B_1 = B_2 -$ is intramolecularly introduced in the polymer chain,
the two different cyclic units, $-B_1 -B_2 -A_1 -A_2 -$ and $-A_1 -A_2 -B_1 -B_2 -$,
respectively, are formed.

Another class of cyclopolymers, of which the structure is not suf-
ficiently characterized by the determination of the residual unsaturation
content, is that obtained from 1,4-dienes. According to the mechanism
proposed for the cyclopolymerization of these monomers [1], bicylic,
monocyclic, and linear structural units can be formed in the course of
the chain growth steps. Since both monocyclic and linear structural units
bear a residual unsaturation, the impossibility of attaining a sufficient
knowledge of the structure of these cyclopolymers through the evaluation
of the residual unsaturations is self-evident.

The above discussion points out that the determination of the cyclo-
polymer composition in terms of structural units often requires additional
information besides knowledge of the residual unsaturation content.

1,5- AND 1,6-DIENES

In the case of the products of the cyclopolymerization of dienes of the
type $A_1 = A_2 - - - - B_2 = B_1$, information in addition to the residual un-
saturation content is obtained from the kinetic relationships between the
mole fractions of the different structural units and the monomer

concentration at which the polymerization was carried out [2], chiefly from knowledge of two parameters, the cyclization ratios $r_{cA}.$ and $r_{cB}.,$ defined as the monomer concentration (or the concentration of both $A_1 = A_2 -$ and $B_1 = B_2 -$) at which radicals $\sim A_1 -\dot{A}_2 - - - - B_2 = B_1$ and $\sim B_1 -\dot{B}_2 - - - - A_2 = A_1$, respectively, can react intramolecularly or inter-molecularly at the same rate. These parameters can be evaluated by determining the mole fractions f_A and f_B of the two residual unsaturations $A_1 = A_2 -$ and $B_1 = B_2 -$ at different monomer concentration (M), through the relationship [2]:

$$(M)[1 - (f_A + f_B)]/f_A = r_{cB}. + r_{cA}.(f_B/f_A)$$

When the cyclization ratios are known, the composition, in terms of the two linear and of the two cyclic structural units, of a cyclopolymer obtained at a given monomer concentration can be completely defined by determining f_U. In fact, considering that f_A and f_B are the mole fractions of linear structural units with a residual unsaturation of type $A_1 = A_2 -$ and $B_1 = B_2 -$, respectively, and taking as f_{Ac} and f_{Bc} the mole fractions of cyclic structural units formed when $A_1 = A_2 -$ and $B_1 = B_2 -$, respectively, are intramolecu-larly introduced into the polymer chain, it is of course:

$$f_A + f_B \quad = f_U$$

$$f_{Ac} + f_{Bc} = 1 - f_U \tag{1}$$

Furthermore, according to our previous treatment [2], the following equations hold:

$$f_{Ac}/f_A = r_{cB}./(M)$$

$$f_{Bc}/f_B = r_{cA}./(M) \tag{2}$$

From Eqs. (1) and (2) one obtains:

$$f_A = \{[(M) + r_{cA}.]f_U - (M)\}/(r_{cA}. - r_{cB}.)$$

$$f_B = \{(M) - [(M) + r_{cB}.]f_U\}/(r_{cA}. - r_{cB}.)$$

$$f_{Ac} = r_{cB}.\{[(M) + r_{cA}.]f_U - (M)\}/(M)(r_{cA}. - r_{cB}.)$$

$$f_{Bc} = r_{cA}.\{(M) - [(M) + r_{cB}.]f_U\}/(M)(r_{cA}. - r_{cB}.) \tag{3}$$

With the aim of illustrating the present method of determination of the composition of cyclopolymers, relationships (3) are applied to the polymers obtained at $60°C$ by free radical initiation from vinyl-trans-crotonate in benzene [3]. The experimental values of (M) and f_U are collected in Table 1. Taking as $A_1 = A_2 -$ the crotonic double bond and as $B_1 = B_2 -$ the vinyl one, we obtained for the cyclization ratios the following values:

$$r_{cA\cdot} = 7.57 \text{ moles/l}$$

$$r_{cB\cdot} = 0.00 \text{ moles/l}$$

Introducing these values, together with the experimental data of Table 1, in Eqs. (3), the mole fractions f_A, f_B, f_{Ac}, and f_{Bc} of the structural units

$$\begin{array}{ll}
\quad | & \quad | \\
CH-O-CO-CH=CH-CH_3 & CH-CO-O-CH=CH_2 \\
\quad | & \quad | \\
CH_2 & CH-CH_3 \\
\quad | & \quad | \\
\end{array}$$

$$\begin{array}{cc}
\mathbf{A} & \mathbf{B}
\end{array}$$

$$\begin{array}{cc}
\begin{array}{c}
CH_3 \\
| \\
CH \\
/ \quad \backslash \\
-CH_2 CH \quad CH- \\
\backslash \quad / \\
O-CO
\end{array}
&
\begin{array}{c}
CH_3 \quad CH_2 \\
| \quad / \quad \backslash \\
-CH-CH \quad CH- \\
\backslash \quad / \\
CO-O
\end{array}
\end{array}$$

$$\begin{array}{cc}
\mathbf{A_c} & \mathbf{B_c}
\end{array}$$
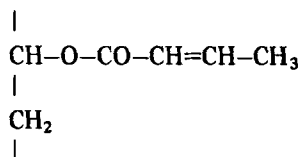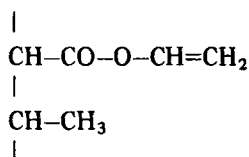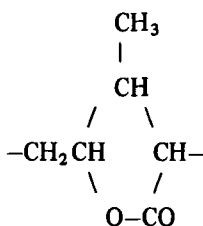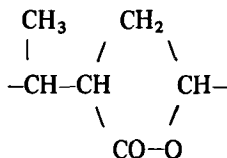
are calculated. The dependence on monomer concentration of the mole fractions of the four different structural units is represented in Fig. 1. A_c structural units are absent in the polymers owing to $r_{cB\cdot} = 0.00$ mole/l.

1,4-DIENES

The determination of the composition, in terms of structural units, of the cyclopolymers obtained from 1,4-dienes can be performed as well by

Table 1. Mole Fractions (f_U) of Residual Unsaturations in the Products of the Free Radical Polymerization at 60°C of Vinyl-trans-crotonate in Benzene-ne Solutions at Different Concentrations (M) [3]

(M) (moles/l)	4.22	2.41	2.11	1.40	0.84	0.45	0.40	0.17
f_U	0.53	0.41	0.38	0.33	0.25	0.19	0.18	0.13

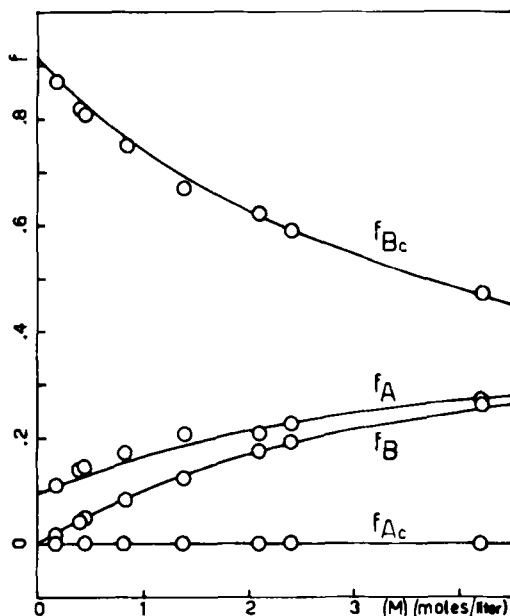Fig. 1. Dependence on monomer concentration of the mole fractions of structural units in the products of the free radical polymerization at 60°C of vinyl-trans-crotonate in benzene. (○): calculated from the values of r_{cA} and r_{cB} and the experimental data of Table 1; the curves are calculated from the kinetic parameters reported in Ref. 3.

employing the kinetic relationships already derived for the particular type of cyclopolymerization these monomers undergo [4]. Such relationships and their application to the polymers from divinyl ether will be reported in the following.

On the basis of telomerization experiments, Aso [5] suggested that, in

the free radical polymerization of divinyl ether, five- and six-membered rings are probably formed. Therefore the structural units collected in Table 2 have to be taken into account. Taking as "monomeric unit" a monomer molecule entered in the polymer chain, it is evident that bicyclic and mono-cyclic structural units are formed by two monomeric units, whereas the linear structural units are formed by only one monomeric unit.
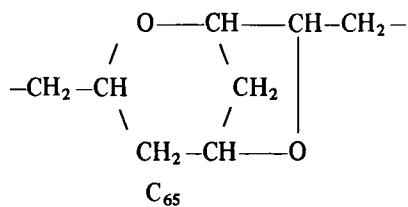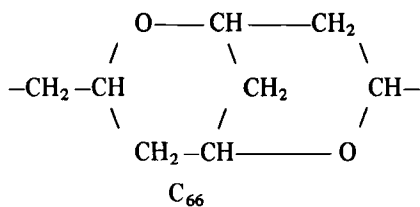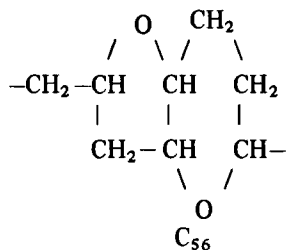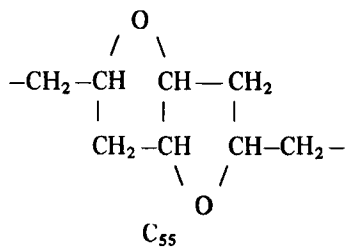
The dependence on monomer concentration of the composition of these cyclopolymers in terms of structural units can be investigated when the composition in terms of monomeric units is known. There are two types of monomeric units: the unsaturated ones (which can form the linear structural units, or can belong to monocyclic structural units) and the saturated ones. These latter, which are always part of a ring, derive from monomer molecules that have contributed to the chain propagation with both their unsaturations.

The reactions leading to the different monomeric (and structural) units are schematically represented in Fig. 2. The solid arrows represent inter-molecular additions of chain radicals on monomer molecules, and the dotted arrows represent cyclization steps. The well-known difficulty of forming a four-membered ring prevents radicals A$\cdot$ from undergoing direct cyclization. These radicals, therefore, transform into radicals B$\cdot$ by an intermolecular ad-dition onto a monomer molecule. Radicals B$\cdot$ can add a monomer molecule, giving again a radical B$\cdot$ (and a linear structural unit is left behind in the chain), or can undergo one of the two cyclizations yielding a five- or a six-membered cylclic radical. Radicals $C_5\cdot$ and $C_6\cdot$ can similarly undergo two different cyclization steps, or add a monomer molecule: in this last case they transform to radicals A$\cdot$. Finally, radicals $C_{55}\cdot$, $C_{56}\cdot$, $C_{65}\cdot$, and $C_{66}\cdot$ can only add a monomer molecule and regenerate radicals A$\cdot$.

The composition of the cyclopolymers will obviously be determined by the competition between the reactions in the scheme. It is easy to see, however, that only radicals B$\cdot$, $C_5\cdot$, and $C_6\cdot$ have the possibility to follow different routes, so that the cyclopolymer composition will depend completely upon the tendency of these radicals to follow different paths. In order to relate the composition of these cyclopolymers to monomer con-centration kinetically, it was found convenient [4, 6] to distinguish the saturated monomeric units formed by primary cyclization of radicals B$\cdot$ from those formed by secondary cyclization of radicals $C_5\cdot$ and $C_6\cdot$. Taking into account all the possible reactions represented in the scheme, we have derived [4] Eqs. (4)-(6) for the relationships between the mole fractions of unsaturated and saturated monomeric units and monomer concentration for the polymers obtained at low conversions.

Table 2. Structural Units Which Can Be Present in the Polymers Obtained by Free Radical Initiation from Divinyl Ether

Bicyclic structural units:

```
         O                              O    CH₂
        / \                            / \ / \
 -CH₂-CH   CH—CH₂              -CH₂-CH   CH   CH₂
    |   |     |                   |   |     |
   CH₂-CH   CH-CH₂-             CH₂-CH    CH-
        \ /                           \ /
         O                             O
        C₅₅                           C₅₆
```

```
    O——CH——CH₂                    O——CH——CH-CH₂-
   /      \    \                  /     \
-CH₂-CH    CH₂   CH-          -CH₂-CH    CH₂     |
   \      /    /                 \     /         |
   CH₂-CH———O                    CH₂-CH——O
       C₆₆                           C₆₅
```

Monocyclic structural units:

```
         O                              O
        / \                            / \
 -CH₂-CH   CH-CH₂-              -CH-CH   CH-
    |        |                    |       |
   CH₂-CH                        CH₂    CH₂
        |                          \    /
        O                           CH
        |                           |
       CH=CH₂                      O-CH=CH₂
        C₅                           C₆
```

Linear structural units:

```
      -CH₂-CH-
          |
          O
          |
        CH=CH₂
          L
```

A•

C₅•   B•   C₆•

C₅₅•   C₅₆•   C₆₅•   C₆₆•

$\sim CH_2-CH\bullet$
|
O
|
(A•) $CH=CH_2$

$\sim CH_2-CH-CH_2-CH\bullet$
| |
O   O
| |
(B•) $CH=CH_2$ $CH=CH_2$

(C₅•)

(C₆•)

(C₅₅•)

(C₅₆•)

(C₆₅•)

(C₆₆•)
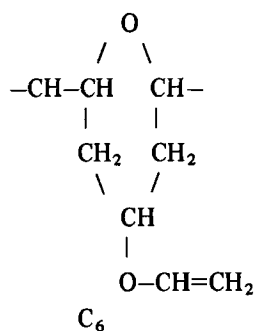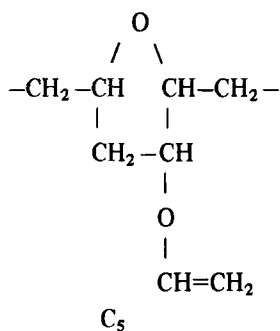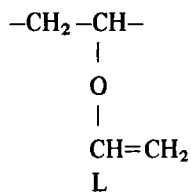
Fig. 2. Possible chain propagation reactions in the free radical polymerization of divinyl ether.

$$f_U = \frac{2(M) + \rho_5 + \rho_6}{2(M) + 2\rho_5 + 2\rho_6} - \frac{\rho_5 \sigma_5}{[2(M) + 2\rho_5 + 2\rho_6][2(M) + \sigma_5]} -$$
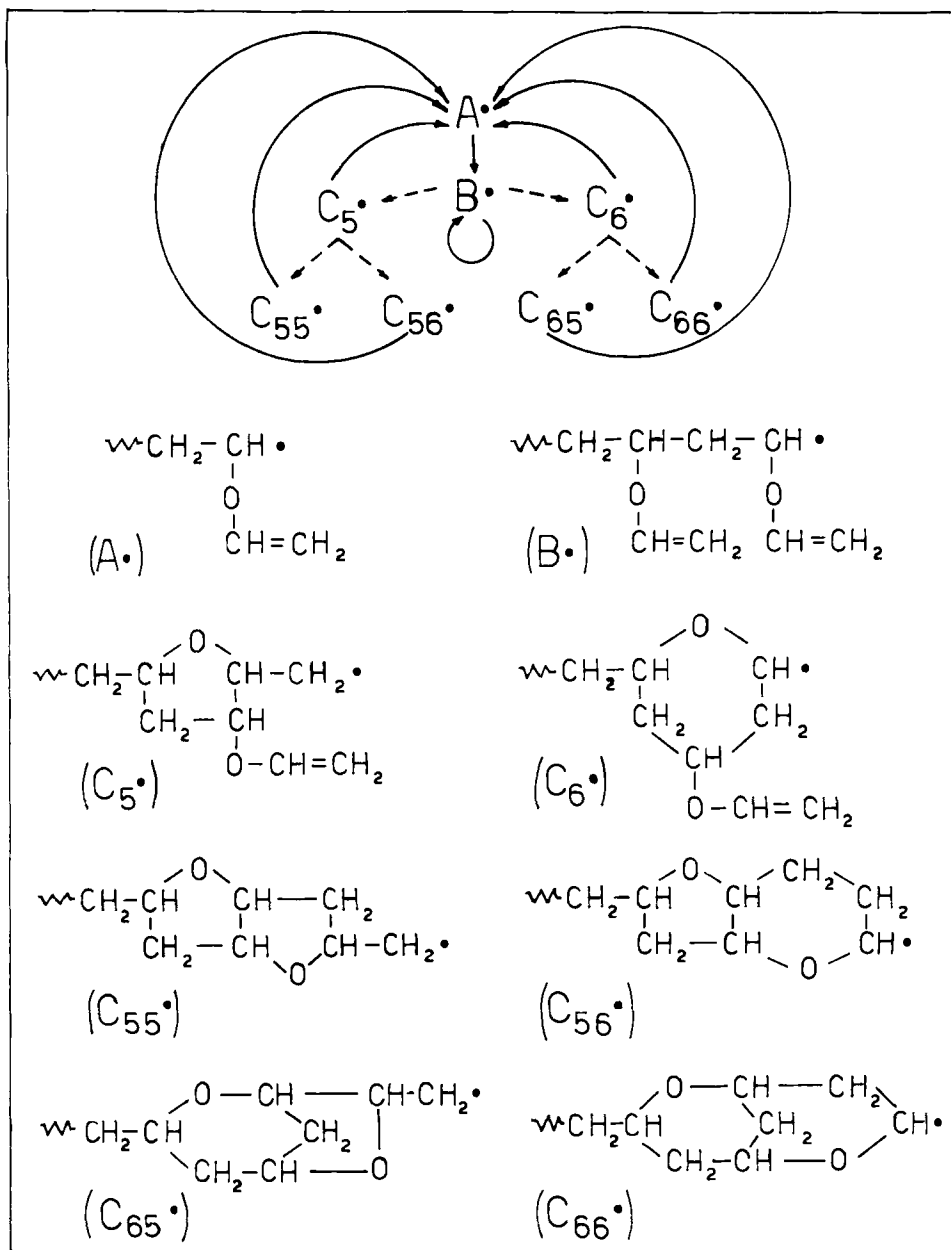
$$\frac{\rho_6 \sigma_6}{[2(M) + 2\rho_5 + 2\rho_6][2(M) + \sigma_6]} \tag{4}$$

$$f_{S1} = \frac{\rho_5 + \rho_6}{2(M) + 2\rho_5 + 2\rho_6} \tag{5}$$

$$f_{S2} = \frac{\rho_5 \sigma_5}{[2(M) + 2\rho_5 + 2\rho_6][2(M) + \sigma_5]} +$$

$$\frac{\rho_6 \sigma_6}{[2(M) + 2\rho_5 + 2\rho_6][2(M) + \sigma_6]} \tag{6}$$

where f_U refers to unsaturated monomeric units, f_{S1} to the saturated ones formed by primary cyclization, and f_{S2} to saturated monomeric units formed by secondary cyclization. The ρ's and σ's are cyclization ratios representing the double bond concentration (twice the monomer concentration when the conversion to polymer is low) at which a cyclizable radical can propagate the chain intramolecularly or intermolecularly at the same rate. ρ_5 and ρ_6 refer to radicals B· giving a five- and a six-membered ring, respectively, and σ_5 and σ_6 to radicals C_5· and C_6·, respectively.

Equations (4), (5) and (6) can be rewritten in the form:

$$f_U = \frac{4(M)^3 + 2(R + S)(M)^2 + (RQ + P)(M)}{4(M)^3 + 2(2R + S)(M)^2 + (2RS + P)(M) + RP} \tag{7}$$

$$f_{S1} = \frac{R}{2[(M) + R]} \tag{8}$$

$$f_{S2} = \frac{R(S - Q)(M) + RP/2}{4(M)^3 + 2(2R + S)(M)^2 + (2RS + P)(M) + RP} \tag{9}$$

where $R = \rho_5 + \rho_6$, $S = \sigma_5 + \sigma_6$, $P = \sigma_5 \sigma_6$, and $Q = (\sigma_5 + \sigma_6 \rho_5 / \rho_6)/(1 + \rho_5/\rho_6)$. The mere determination of f_U in the polymers obtained at different known monomer concentrations allows the evaluation of R, S, P, and Q. By introducing these quantities into Eqs. (8) and (9), one can calculate the mole fractions f_{S1} and f_{S2} of the two types of saturated

monomeric units. The composition of the cyclopolymers, in terms of monomeric units, is thus completely defined. The cyclopolymer composition in terms of structural units can now be calculated by means of Eqs. (10)-(12) [4], relating the mole fractions of monomeric and structural units:

$$f_L = [f_U - (f_{S1} - f_{S2})]/(f_U + f_{S2}) \qquad (10)$$

$$f_{C1} = (f_{S1} - f_{S2})/(f_U + f_{S2}) \qquad (11)$$

$$f_{C2} = f_{S2}/(f_U + f_{S2}) \qquad (12)$$

where f_U, f_{C1}, and f_{C2} are the mole fractions of linear, monocyclic, and bicyclic structural units, respectively. It is, however, possible to attain a more detailed knowledge of the structure of the cyclopolymers if some hypotheses can be made about the relative tendency toward cyclization of radicals $C_5 \cdot$ and $C_6 \cdot$. In this case it becomes possible to distinguish which of the two interchangeable pairs of values of the σ's obtained from S and P has more likelihood to be the correct one, and consequently to calculate from Q a single value for ρ_5/ρ_6. Knowing σ_5, σ_6, and ρ_5/ρ_6, one can calculate at a given monomer concentration the structure of the cyclopolymers from divinyl ether in terms of the mole fractions of linear structural units (f_L), of monocyclic units with a five- and a six-membered ring, respectively (f_{C5} and f_{C6}), of bicyclic units deriving from $C_5 \cdot$ radicals ($f_{C55} + f_{C56}$), and of bicyclic units deriving from $C_6 \cdot$ radicals ($f_{C65} + f_{C66}$). In fact, one can easily realize that the following four simultaneous equations hold:

$$f_{C5} + f_{C6} + f_{C55} + f_{C56} + f_{C65} + f_{C66} = 1 - f_L = f_{S1}/(f_U + f_{S2})$$
$$(f_{C5} + f_{C55} + f_{C56})/(f_{C6} + f_{C65} + f_{C66}) = \rho_5/\rho_6$$
$$(f_{C55} + f_{C56})/f_{C5} = \sigma_5/2(M)$$
$$(f_{C65} + f_{C66})/f_{C6} = \sigma_6/2(M)$$

Solving for f_{C5}, f_{C6}, $(f_{C55} + f_{C56})$, and $(f_{C65} + f_{C66})$, one obtains:

$$f_{C5} = \frac{2(M)\rho_5/\rho_6}{[2(M) + \sigma_5](1 + \rho_5/\rho_6)} \cdot \frac{f_{S1}}{f_U + f_{S2}}$$

$$f_{C6} = \frac{2(M)}{[2(M) + \sigma_6](1 + \rho_5/\rho_6)} \cdot \frac{f_{S1}}{f_U + f_{S2}} \qquad (13)$$

$$f_{C55} + f_{C56} = \frac{\sigma_5\rho_5/\rho_6}{[2(M) + \sigma_5](1 + \rho_5/\rho_6)} \cdot \frac{f_{S1}}{f_U + f_{S2}}$$

$$f_{C65} + f_{C66} = \frac{\sigma_6}{[2(M) + \sigma_6](1 + \rho_5/\rho_6)} \cdot \frac{f_{S1}}{f_U + f_{S2}}$$

Equation (4) was applied to the results of the determination of the residual unsaturations in the products of the free radical polymerization at 70°C of divinyl ether in benzene (Table 3) [4] and by means of a nonlinear least square method [7], the following parameters were obtained:

$$R = \rho_5 + \rho_6 > 200 \text{ moles/1}$$
$$S = \sigma_5 + \sigma_6 = 12.71 \text{ moles/1}$$
$$P = \sigma_5\sigma_6 = 15.24 \text{ (moles/1)}^2$$
$$Q = (\sigma_5 + \sigma_6\rho_5/\rho_6)/(1 + \rho_5/\rho_6) = 6.01 \text{ moles/1}$$

The value of R obviously means that, in the usual range of monomer concentrations, radicals B· practically disappear only by cyclization and not by reaction with monomer. By assuming $\sigma_5 > \sigma_6$ one calculates:

$$\sigma_5 = 11.37 \text{ moles/1}$$
$$\sigma_6 = 1.34 \text{ moles/1}$$
$$\rho_5/\rho_6 = 1.15$$

The fact that ρ_5/ρ_6 is so close to 1 indicates that radicals B· display almost the same tendency to yield C_5· and C_6· radicals, and consequently both five- and six-membered rings are formed in the course of the free radical

Table 3. Mole Fractions (f_U) of Unsaturated Monomeric Units,
as Determined Spectrophotometrically and Chemically, in the
Products of the Free Radical Polymerization at 70°C of
Divinyl Ether in Benzene Solutions at Different
Concentrations (M) [4].

(M) (moles/1)	f_U (IR)	f_U (chem)	(M) (moles/1)	f_U (IR)	f_U (chem)
0.78	0.16	--	2.38	0.26	0.28
1.08	0.17	0.20	2.48	–	0.29
1.31	0.20	0.22	2.58	0.25	–
1.37	0.20	–	3.43	0.28	–
1.47	0.22	0.22	3.64	0.31	0.32
1.58	0.21	–	3.67	0.31	–
1.80	0.23	0.26	4.07	0.30	–
1.90	0.22	–	4.17	0.31	–
2.30	0.24	–			

polymerization of divinyl ether. It is of interest to note that this conclusion
is practically independent of the hypothesis that σ_5 is greater than σ_6: in
fact, by interchanging the above values of these two cyclization ratios, one
obtains $\rho_5/\rho_6 = 0.87$, which is again close to 1. These results give more
confidence to the conclusions drawn by Aso [5] from telomerization experi-
ments, whose extrapolation to polymerization products suffers, in general,
of some arbitrariness.

It is easy to see from Eqs. (8) and (9) that when, as in the present case,
R largely exceeds the highest monomer concentrations at which polymeriza-
tions were carried out, the values of S, P, and Q are sufficient to calculate
the mole fractions f_{S1} and f_{S2} of saturated monomeric units derived from
monomer molecules which have introduced in the polymer chain their
second unsaturation in a primary and in a secondary cyclization reaction,
respectively. The dependence on monomer concentration of the (calculated)
mole fractions f_{S1} and f_{S2} is represented in Fig. 3, together with that of the
(experimental) mole fraction f_U.

We can now evaluate the cyclopolymer composition in terms of structural
units, by introducing into Eqs. (10) and (13) the values of ρ_5/ρ_6, σ_5, and
σ_6, together with those of f_U, f_{S1}, and f_{S2} at different monomer concen-
trations, as obtained from Fig. 3. The dependence on monomer concentra-
tion of the mole fractions of linear, monocyclic, and bicyclic structural units
is represented in Fig. 4. It may be of interest to note that if σ_5 is smaller
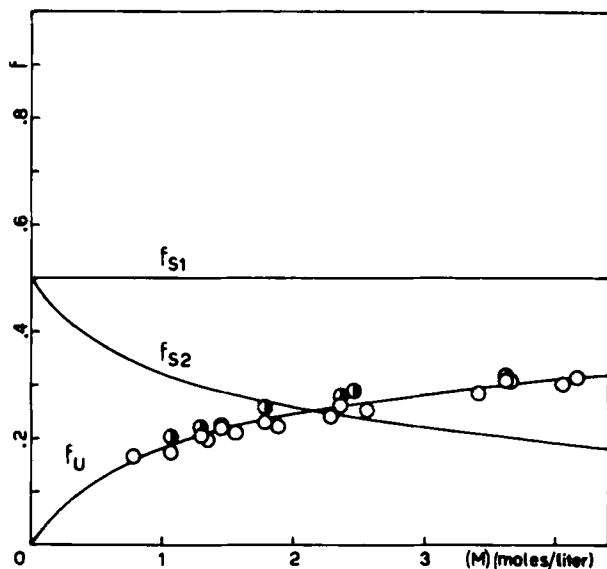
Fig. 3. Dependence on monomer concentration of the mole fractions of monomeric units in the polymers obtained by free radical initiation at 70°C from divinyl ether in benzene. (○, ◑): experimental points from Table 3; the curves are calculated according to Eqs. (8) and (9).

than σ_6 the diagram would not be altered, but the curves relative to f_{C5} and f_{C6}, as well as those relative to $f_{C55} + f_{C56}$ and $f_{C65} + f_{C66}$, are interchanged. In any case, it is evident from Fig. 4 that the linear structural units are absent in the free radical polymerization products of divinyl ether at 70°C in benzene, as an obvious consequence of the large values of ρ_5 and ρ_6, and consequently the residual unsaturations in the polymers belong exclusively to monocyclic structural units.

CONCLUSIONS

The above discussion points out that a deep insight into the cyclopolymer composition is made possible by the investigation of the dependence on monomer concentration of the residual unsaturation content, and particularly by a knowledge of the cyclization ratios. Obviously some structural questions, such as the determination of the ring size in the polymers from 1,5- and 1,6-dienes, or the separate evaluation of the mole fractions of the
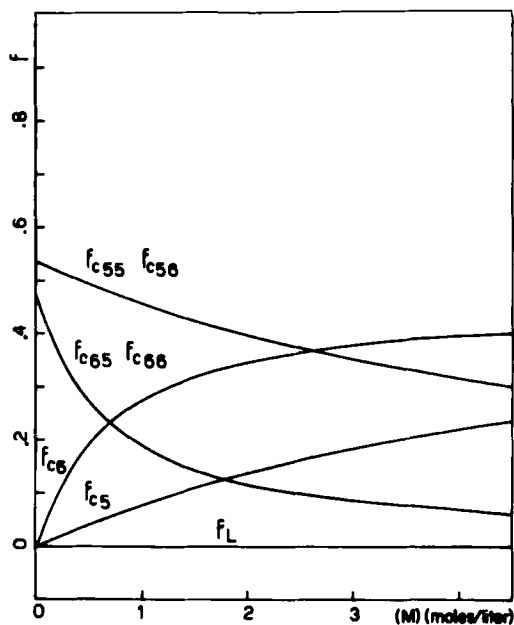
Fig. 4. Dependence on monomer concentration of the mole fractions of structural units in the polymers obtained by free radical polymerization at 70°C from divinyl ether in benzene, as calculated from Eqs. (10) and (13).

two bicyclic structural units deriving from radicals of type of $C_5 \cdot$ and $C_6 \cdot$ in the polymers from 1,4-dienes, still remain without an answer. The resolution of these problems, however, requires very elaborate analytical techniques, whereas the method of determination of cyclopolymer composition presented here involves only the usually simple evaluation of the content of residual unsaturations. Moreover, the knowledge of kinetic parameters, such as the cyclization ratios, allows a quantitative comparison of the behavior of different monomers toward cyclopolymerization, and can contribute to a full interpretation of this polymerization process.

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REFERENCES

[1] E. Y. C. Chang and C. C. Price, *J. Amer. Chem. Soc.*, **83**, 4650 (1961); M. G. Avetyan, E. G. Darbinyan, A. A. Saakyan, F. S. Kinoyan, and S. G. Matsoyan, *Polym. Sci.* (USSR) (English Transl), **6**, 1 (1964); C. Aso and S. Ushio, *Kogyo Kagaku Zasshi,* **65**, 2085 (1962).

[2] L. Trossarelli, M. Guaita, and A. Priola, *Ric. Sci.,* **35** (II-A), 379 (1965); *J. Polym. Sci., Part C,* **16**, 4713 (1969).

[3] L. Trossarelli and M. Guaita, *Polymer,* **9**, 233 (1968).

[4] M. Guaita, G. Camino, and L. Trossarelli, *Makromol. Chem.,* **131**, 237 (1970).

[5] C. Aso, S. Ushio, and M. Sogabe, *Makromol. Chem.,* **100**, 100 (1967).

[6] M. Guaita, G. Camino, and L. Trossarelli, *Makromol. Chem.,* **130**, 243 (1969).

[7] R. H. Pennington, *Introductory Computer Methods and Numerical Analysis,* Macmillan, New York, 1965, p. 382.