Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Cyclocopolymerization of Divinyl Sulfone with Vinyl Ethers

K. Fujimori[a]
[a] Department of Physical and Inorganic Chemistry, The University of New England, Armidale, N. S. W., Australia

To cite this Article Fujimori, K.(1976) 'Cyclocopolymerization of Divinyl Sulfone with Vinyl Ethers', Journal of Macromolecular Science, Part A, 10: 6, 1005 — 1015
To link to this Article: DOI: 10.1080/00222337608061232
URL: http://dx.doi.org/10.1080/00222337608061232

J. MACROMOL. SCI.-CHEM., A10(6) pp. 1005-1015 (1976)

Cyclocopolymerization of Divinyl Sulfone with Vinyl Ethers

K. FUJIMORI

Department of Physical and Inorganic Chemistry
The University of New England
Armidale, N.S.W., 2351, Australia

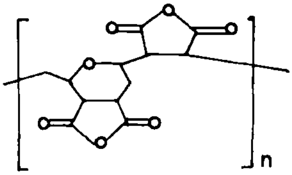
ABSTRACT

The radical copolymerization of divinyl sulfone (DVS) with ethyl vinyl ether (EVE) and 2,3-dihydropyran (DHP) gave soluble copolymers of composition between 1:1 and 1:2 richer in vinyl ether content in a wide range of monomer feed compositions even though the vinyl ethers did not homopolymerize. Because almost no residual double bonds were detected in the copolymers, the copolymerization was interpreted as a cyclocopolymerization, falling in the category where the diene homopropagated but the monoolefin did not. The reactivity ratios of the cyclocopolymerization were determined to be $R_1 = 0.02$ and $R_C = 3.0$ for the DVS-EVE copolymerization, and $R_1 = 0.02$ and $R_C = 5.0$ for the DVS-DHP copolymerization. Formations of 1:1 charge transfer complex were detected in the UV region, the maximum absorptions being at 39,350 cm^{-1} for the DVS-EVE complex and 39,050 cm^{-1} for the DVS-DHP complex in chloroform at 23°C. The great deviation from the classical binary copolymerization equation based on the Q-e scheme

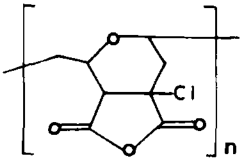
suggested the participation of the complexation of the monomers. On the other hand, the classical copolymerization equation predicted the composition of the DVS-acrylonitrile copolymer formed by the random cyclocopolymerization very well. No charge transfer complex was found in chloroform for the DVS-acrylonitrile pair.

INTRODUCTION

The radical copolymerization of 1,4-diene with monoolefin has been shown [1] to consist of the intermolecular catenization and the intramolecular cyclization. It has been proposed [2-4] that the constant 1:2 and 1:1 repeating units are formed when copolymers of divinyl ether with maleic anhydride (I) and chloromaleic anhydride (II) are formed through the charge transfer (CT) complex of the monomers.



I



II

The composition equation (1) based on the cyclocopolymerization mechanism was derived by Barton, Butler, and Chapin [5].

$$n = \frac{(1+R_1x)\{1/[M_2] + (1/a)(1+x/R_3)\}}{(1/a)\{(x/R_3)+(R_2/x)+2\}+(1/[M_2])\{1+(1+R_2/x)(1+R_cx)^{-1}\}} \qquad (1)$$

Here M_1 is the diene, M_2 is the monoolefin, $n = d[M_1]/d[M_2]$ and $x = [M_1]/[M_2]$. R_1, R_2, and R_c are the reactivity ratios for the propagation step of diene, monoolefin, and cyclized radicals, respectively.

Divinyl sulfone (DVS) ($e = 1.33$, $Q = 0.14$ [6]) was copolymerized with ethyl vinyl ether (EVE) ($e = -1.17$, $Q = 0.022$ [7]) and 2,3-dihydropyran (DHP) ($e = -0.93$, $Q = 0.013$ [8]). It was expected that cyclocopolymerization would occur, being assisted by the difference in the monomer polarities. The copolymerization was compared with the random copolymerization of DVS with acrylonitrile (AN) ($e = 1.20$, $Q = 0.60$ [7]).

The classical binary composition equation assumes a random mechanism. When a diene is a monomer, the diene concentration has to be multiplied by 2 to take account of the enhanced probability of the reaction [6, 9]:

$$\frac{d[M_1]}{d[M_2]} = \frac{2[M_1]}{[M_2]} \frac{(2r_1[M_1]/[M_2]) + 1}{(2[M_1]/[M_2]) + r_2} \tag{2}$$

where r_1 and r_2 are the reactivity ratios of diene and monoolefin radicals, respectively.

RESULTS AND DISCUSSION

The results of the copolymerization carried out in benzene are given in Tables 1 and 2. The copolymer composition based on the sulfur analysis is shown in Figures 1 and 2. The copolymers precipitated from benzene solution as the polymerization proceeded but the purified copolymers were soluble in N,N-dimethylformamide (DMF). When the copolymerization was carried out in DMF no precipitation occurred. The C=C stretching of DVS at 1605 cm^{-1}, of EVE at 1615 cm^{-1}, and of DHP at 1645 cm^{-1}, and sp^2 C–H stretching of DVS at 3060 cm^{-1}, of EVE at 3160 cm^{-1}, and of DHP at 3080 cm^{-1} were almost absent in the infrared spectra of the copolymers. The copolymers showed absorptions of the sulfone group at 1120 and 1300 cm^{-1} and the ether linkages at 1090 cm^{-1} (DVS-EVE copolymer) and at 1080 cm^{-1} (DVS-DHP copolymer). DVS homopolymerized to a crosslinked polymer, while EVE and DHP would not homopolymerize under the conditions used for the copolymerization. Two features are apparent in Figs. 1 and 2, viz., the copolymers incorporated over 50% of the unhomopolymerizable vinyl ethers over a wide range of monomer feed composition, and secondly, the copolymer composition was mostly between 1:1 and 1:2 (diene:monoolefin). The above observations can be explained if the copolymerization of DVS with vinyl ethers is a cyclocopolymerization which gives copolymers composed of a mixture of the structures similar to I and II. This copolymerization forms another category of cyclocopolymerization in which diene can homopropagate ($R_1 \neq 0$) but the monoolefin does not ($R_2 \cong 0$). This is in addition to the three categories, proposed by Barton et al. [5] which were designated (a), (b) and (c). If the cyclization is complete ($K_C \gg K_{32}$), the Eq. (1) reduces to

$$n = \frac{(1 + R_1x)(1 + R_Cx)}{(R_Cx + 2)} \tag{3}$$

TABLE 1. Copolymerization of Divinyl Sulfone (M_1) with Ethyl Vinyl Ether (M_2)[a]

Mole fraction of EVE in feed	Conversion (wt %/min)	S (%)	Mole fraction of EVE in copolymer
0.10	2.18/ 83	18.01	0.454
0.20	2.10/ 114	16.61	0.509
0.35	11.07/ 810	16.68	0.507[b]
0.40	6.34/ 460	15.29	0.559
0.50	9.85/1110	15.70	0.544
0.60	6.18/ 560	15.29	0.559
0.65	6.96/ 990	14.62	0.584
0.80	6.02/1143	13.78	0.614[c]
0.85	4.21/ 790	13.80	0.613
0.90	5.90/1142	13.87	0.610

[a] [DVS + EVE] = 1.47 mole/liter, [BPO] = 1.47×10^{-2} mole/liter; 60°C; in benzene.

[b] Relative viscosity = 1.037.

[c] Relative viscosity = 1.045.

For each experimental value of n and x, the plot of R_1 against R_c gave a curved line. The most probable R_1 and R_c values were chosen from the intercepts of these curved lines and further improved by the curve fitting method. The solid lines in Figs. 1 and 2 were drawn for $R_1 = 0.02$ and $R_c = 3.0$ for the DVS-EVE copolymerization and for $R_1 = 0.02$ and $R_c = 5.0$ for the DVS-DHP copolymerization.

The reaction sequences of the DVS-vinyl ether cyclocopolymerization may be shown by Eqs. (4), (5), and (6) in which the K are the rate constants and the m are the growing radical species. The reactivity ratios in Eq. (1) are defined as $R_1 = K_{11}/K_{12}$, $R_2 = K_{22}/K_{21}$, $R_c = K_{c1}/K_{c2}$, and $a = K_c/K_{32}$. The small R_1 values in this cyclocopolymerization indicated a strong alternating tendency of the DVS radical toward vinyl ethers. When R_1 was very small, the combination of reactions (5) and (6) would lead to copolymer compositions between 1:1 and 1:2 as observed in this experiment, the extent of the combination being indicated by R_c. The reciprocal of R_c is a measure of the reactivity of the monoolefin (M_2) toward the cyclized DVS radical (m_c), which is a positively polarized radical, when a common

TABLE 2. Copolymerization of Divinyl Sulfone (M_1) with 2,3-Dihydropyran (M_2)[a]

Mole fraction of DHP in feed	Temp (°C)	AIBN × 10^2 (mole/liter)	Conversion (wt %/min)	S (%)	Mole fraction of DHP in copolymer
0.10	70	2.03	3.76/ 10	16.70	0.467
0.15	60	1.47	9.47/ 240	16.62	0.471
0.30	60	1.47	10.34/ 860	15.41	0.517[b]
0.35	70	2.03	12.59/1440	14.62	0.545
0.50	60	1.47	5.88/ 865	15.07	0.529[c]
0.65	70	2.03	5.62/1440	13.27	0.594
0.70	60	1.47	3.61/ 870	14.63	0.546
0.85	60	1.47	1.68/ 880	13.53	0.586
0.90	70	2.03	1.55/1230	13.05	0.602

[a] [DVS + DHP] = 1.47 mole/liter; in benzene.

[b] Relative viscosity = 1.027.

[c] Relative viscosity = 1.016.

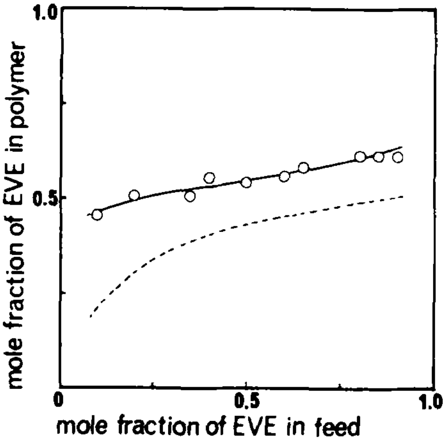


FIG. 1. Copolymer composition curves for the copolymerization of DVS with EVE: (- -) calculated by Eq. (2) for random copolymerization for r_1(DVS) = 0.158 and r_2(EVE) = 0.012 based on the reported Q and e values; (—) calculated by Eq. (3) for cyclocopolymerization for R_1 = 0.02 and R_c = 3.0.

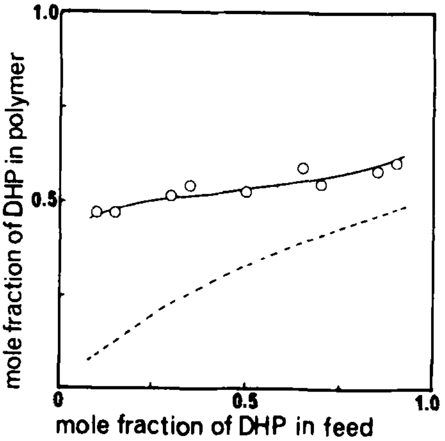
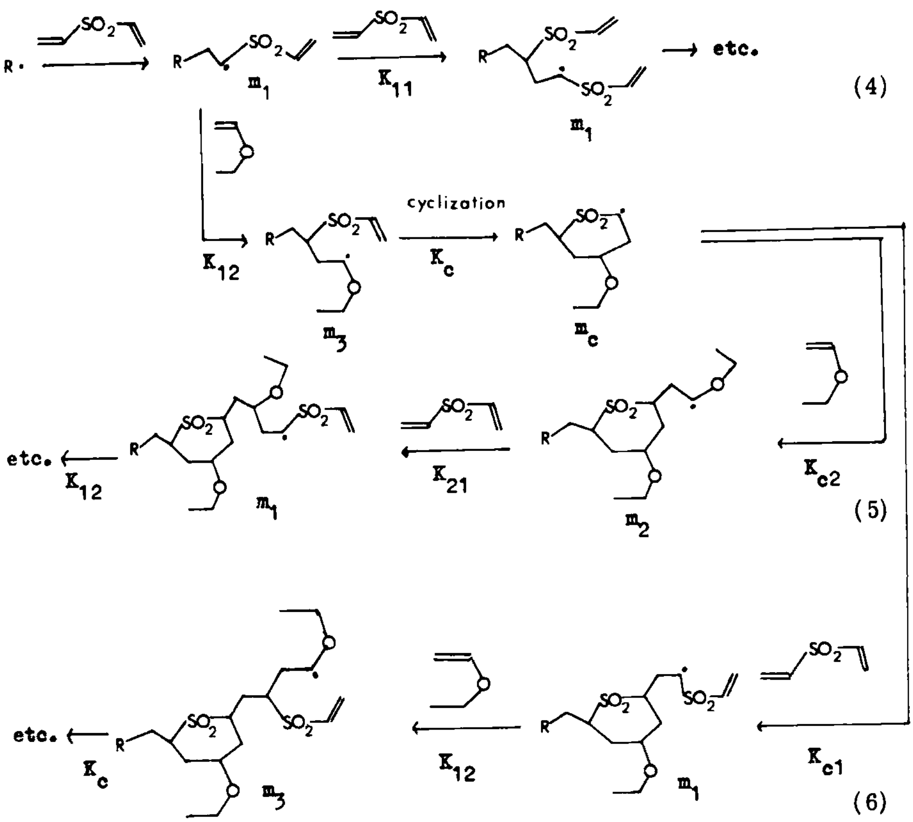


FIG. 2. Copolymer composition curves for the copolymerization of DVS with DHP: (- -) calculated by Eq. (2) for random copolymerization for r_1(DVS) = 0.533 and r_2(DHP) = 0.011 based on the reported Q and e values; (—) calculated by Eq. (3) for cyclocopolymerization for R_1 = 0.02 and R_c = 5.0.

diene (M_1) is used. The larger $1/R_c$ value of DVS-EVE system is in agreement with the larger negative e value of EVE monomer than that of DHP.



It is interesting to note that Eq. (3) predicted a limit of n → 1/2 as x → 0, which appeared to be the case in this experiment, while the classical random copolymerization equation, Eq. (2), predicted a limit of n → 1 as x → 0 when r_2 was small as shown by the broken lines in Figures 1 and 2. The r_1 and r_2 values in Eq. (2) were calculated by Eqs. (7) and (8) by using the reported Q and e values of the monomers [10].

$$r_1 = (Q_1/Q_2)\exp\{-e_1(e_1 - e_2)\} \tag{7}$$

$$r_2 = (Q_2/Q_1)\exp\{-e_2(e_2 - e_1)\} \tag{8}$$

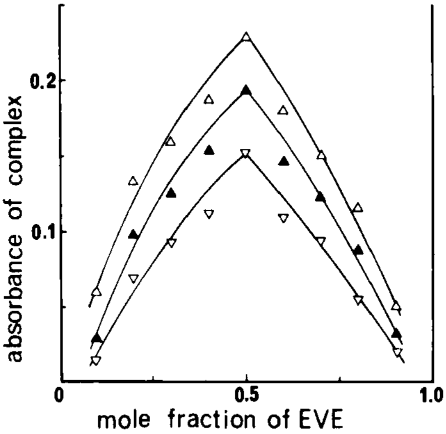


FIG. 3. Ultraviolet determination of stoichiometry of CT complex of DVS with EVE: (△) at 39,400 cm^{-1}; (▲) at 39,000 cm^{-1}; (▽) at 38,600 cm^{-1}. In $CHCl_3$ at 23°C, [DVS + EVE] = 1.65×10^{-3} mole/liter.

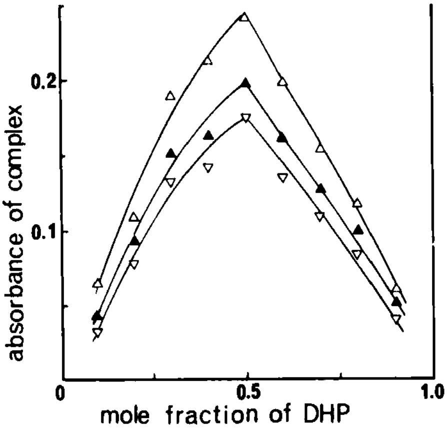


FIG. 4. Ultraviolet determination of stoichiometry of CT complex of DVS with DHP: (△) at 38,600 cm^{-1}; (▲) at 38,200 cm^{-1}; (▽) at 38,000 cm^{-1}. In $CHCl_3$ at 23°C, [DVS + DHP] = 1.65×10^{-3} mole/liter.

Inadequacy of the random treatment was obvious. The enhanced reactivity of vinyl ethers undergoing cyclocopolymerization with DVS suggested a similarity to divinyl ether-maleic anhydride cyclocopolymerization, in which the participation of the charge-transfer (CT) complex formed between the comonomers was proposed [2-4].

The CT complexation of DVS with the vinyl ethers was detected in the UV region in chloroform at 23°C, the maximum absorptions being at 39,350 cm^{-1} for the DVS-EVE complex and at 39,050 cm^{-1} for the DVS-DHP complex. The vinyl ethers were thought to be the donors and DVS the acceptor. The stoichiometry of the complexation in chloroform determined by the continuous variation method [11] was found to be 1:1 for both complexes, as shown in Figs. 3 and 4. The absorbances which were due solely to the complexes were plotted against the composition of the donors at various wave numbers. The very small R_1 values (even though DVS homopolymerizes) and the almost complete cyclization may correspond to a semiconcerted cyclization mechanism, which involves a pre-orientation of monomers through the CT complex as proposed by Butler et al. [2].

To see the effect of the molecular association, the composition of the DVS-AN copolymer (Table 3) was compared with the prediction by the random treatment by Eq. (2), which is shown by the broken line in Fig. 5. The agreement with the experimental results is excellent, contrasting with the great discrepancies in the curves representing the copolymerization of DVS with vinyl ethers. There was no CT complexation detectable for the DVS-AN pair in the UV range in chloroform. However, the copolymer was soluble in DMF, and its IR spectrum showed very little residual C=C double bond, indicating almost complete cyclization as pointed out by Butler and Kasat [12].

TABLE 3. Copolymerization of Divinyl Sulfone (M_1) with Acrylonitrile (M_2)[a]

Mole fraction of AN in feed	Conversion (wt %/3 hr)	S (%)	Mole fraction of AN in copolymer
0.15	2.64	22.80	0.297
0.30	2.07	20.19	0.434
0.50	1.75	11.81	0.743
0.70	1.69	8,96	0.819
0.85	3.83	2.22	0.962

[a] [DVS + AN] = 1.47 mole/liter, [AIBN] = 1.47 × 10^{-2} mole/liter; 60°C; in benzene.

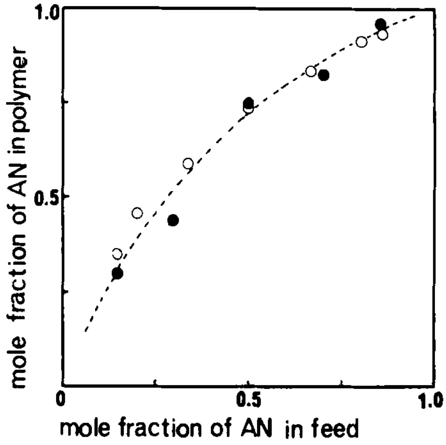


FIG. 5. Copolymer composition of DVS-AN copolymer: (●) by sulfur analysis; (○) by nitrogen analysis according to Butler and Kasat [12]; (- -) calculated by Eq. (2) for a random copolymerization for r_1(DVS) = 0.176 and r_2(AN) = 5.45 based on the reported Q and e values.

The cyclization may have occurred in a random fashion without the involvement of the pre-association of the monomers because of the convenient proximity of the pendent double bond of the penultimate DVS unit to the growing AN radical.

EXPERIMENTAL

Polymerizations were carried out in glass tubes of 30 cc capacity immersed in an oil thermostat. The tubes were initially sealed under high vacuum after freeze-thaw degassing. Polymers were purified by reprecipitating DMF solution in dry diethyl ether. The sulfur content of the DVS-EVE and DVS-DHP copolymers was determined by Shöniger's method, in which about 10 mg of the sample was burned in oxygen with H_2O_2; and resultant sulfuric acid was titrated with 0.01 M NaOH by high-frequency conductometric titration with a Philips PR 9500 bridge. The sulfur content of DVS-AN copolymer was determined by titrating the sulfate complexometrically with 0.01 M $BaCl_2$ and 0.01 M EDTA, Eriochrome Black T being used as the indicator [13]. A Unicam SP 200 infrared spectrophotometer and a Unicam SP 700C ultraviolet spectrophotometer were used. Viscosity was measured with an Ostwald-Fenske viscometer in DMF at 25°C, the concentration being 0.5 g/dl.

REFERENCES

[1] G. B. Butler, paper presented at American Chemical Society Meeting, San Francisco, April 1958; Abstracts, 6R; J. Polym. Sci., 48, 279 (1960).
[2] G. B. Butler and K. C. Joyce, J. Polym. Sci. C, 22, 45 (1968).
[3] G. B. Butler and A. F. Campus, J. Polym. Sci. A-1, 8, 545 (1970).
[4] L. J. Guibault and G. B. Butler, J. Macromol. Sci.-Chem., A5, 1219 (1971).
[5] J. M. Barton, G. B. Butler, and E. C. Chapin, J. Polym. Sci. A, 3, 501 (1965).
[6] E. Y. C. Chang and C. C. Price, J. Amer. Chem. Soc., 83, 4650 (1961).
[7] G. E. Ham, Ed., Copolymerization, Wiley-Interscience, New York, 1964, p. 845.
[8] K. Fujimori, J. Macromol. Sci.-Chem., A9, 495 (1975).
[9] R. H. Wiley and E. E. Sales, J. Polym. Sci., 42, 491 (1960).
[10] T. Alfrey, Jr. and C. C. Price, J. Polym. Sci., 2, 101 (1946).
[11] P. Job, C. R. Acad. Sci. (Paris), 180, 928 (1925); Ann. Chim. Phys., 9, 113 (1928).
[12] G. B. Butler and R. B. Kasat, J. Polym. Sci. A, 3, 4205 (1965).
[13] W. Schöniger, Mikrochim. Acta, 1956, 869.

Accepted by editor October 2, 1975
Received for publication October 27, 1975