

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Studies in Cyclocopolymerization. XIII. A Study of Steric Effects in Cyclocopolymerization of Divinyl Ether with Substituted Electron-Acceptor Alkenes

Kiyohisa Fujimori^a; George B. Butler^a

^a Department of Chemistry, University of Florida, Gainesville, Florida

To cite this Article Fujimori, Kiyohisa and Butler, George B.(1973) 'Studies in Cyclocopolymerization. XIII. A Study of Steric Effects in Cyclocopolymerization of Divinyl Ether with Substituted Electron-Acceptor Alkenes', *Journal of Macromolecular Science, Part A*, 7: 2, 415 – 432

To link to this Article: DOI: 10.1080/00222337308061147

URL: <http://dx.doi.org/10.1080/00222337308061147>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

**Studies in Cyclocopolymerization. XIII.
A Study of Steric Effects in
Cyclocopolymerization of Divinyl Ether
with Substituted Electron-Acceptor Alkenes**

KIYOHISA FUJIMORI and GEORGE B. BUTLER

Department of Chemistry
University of Florida
Gainesville, Florida 32601

ABSTRACT

The equilibrium constants for charge-transfer (CT) complex formation between divinyl ether (DVE) and several substituted maleic anhydrides and 2-cyclopentene-1,4-dione were measured in CHCl_3 by use of UV spectroscopy. The copolymerization of DVE with these acceptor monoolefins produced regular cyclocopolymers of constant 1:1 or 1:2 (DVE:monoolefin) composition regardless of the feed composition. Comparison of the CT complexation and the cyclocopolymerization leads to the following conclusions: 1) A strong CT complex gives regular cyclocopolymer of constant 1:1 composition having a copolymer backbone made up of only 1,4-diene units; 2) when a monoolefin is unreactive (often sterically), the 1:1 cyclocopolymer is produced; and 3) if CT complexation is weak and the monoolefin is reactive toward radicals (but not so reactive as to homopolymerize easily), a 1:2 alternating cyclocopolymer is produced. A facile and quantitative elimination of hydrogen halides with dilute aqueous NaOH solution was found.

Comparison of the elimination reactions for DVE-chloromaleic anhydride, DVE-bromomaleic anhydride, and DVE-dichloromaleic anhydride 1:1 regular alternating cyclocopolymers leads to a conclusion which supports the six-membered ring structure of the repeating cyclic unit formed through the intramolecular cyclization in the cyclocopolymerization.

INTRODUCTION

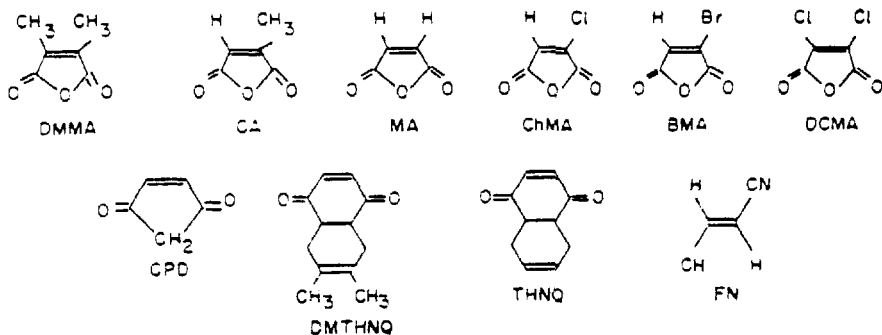
It was pointed out by Kokubo, Iwatsuki, and Yamashita that there is a parallel tendency between the strength of the charge-transfer (CT) complex of a donor-acceptor pair of comonomers and the alternating tendency in their copolymerization [1]. In the cyclocopolymerization of donor 1,4-dienes with acceptor monoolefins, alternating cyclocopolymers having 1:2 (diene:monoolefin) composition were obtained for the donor-acceptor pairs of divinyl ether (DVE)-maleic anhydride (MA) [2], DVE-fumaronitrile (FN) [3], and 1,4-pentadiene-MA [3]. Participation of a CT complex formed between the donor 1,4-diene and the acceptor monoolefin was proposed to explain the alternating copolymerization [4]. However, it has been known for some time that the composition of the alternating cyclocopolymers are 1:2 (diene:monoolefin), while the stoichiometry of the CT complexes are always 1:1 [4c]. An "alternating copolymerization" of a CT complex and a free monoolefin was proposed as an explanation [5]. The donor-acceptor pair of DVE-2-cyclopentene-1,4-dione (CPD) was the first to be found to form a regular 1:1 cyclocopolymer [6]. It has been shown recently that when an acceptor monoolefin is highly sterically hindered and hence much less reactive in the "alternating copolymerization of CT complex with a free monoolefin," a regular 1:1 cyclocopolymer was obtained, apparently through a "homopolymerization" of the CT complex. Tetrahydronaphthoquinone (THNQ) and dimethyltetrahydronaphthoquinone (DMTHNQ) were examples of such highly hindered acceptor monoolefins [7]. The DVE-chloromaleic anhydride (ChMA) pair was also found to form a regular 1:1 cyclocopolymer [8]. It has also been shown that a better electron acceptor produced a more alternating cyclocopolymer, most probably through stronger CT complexation [9].

It is the purpose of this paper to present evidence that a strong CT complex (judging from the equilibrium constant of complexation, K), and/or low reactivity of the free monoolefin (often sterically) will lead to a cyclocopolymer of regular 1:1 composition having a copolymer backbone made up of only 1,4-diene units.

RESULTS AND DISCUSSION

Charge-Transfer Complex and Copolymer Composition

DVE was chosen as the donor 1,4-diene and derivatives of maleic anhydride were used predominantly as the acceptor monoolefins because comparison was easier by using structurally related model compounds. Chloroform was used as the solvent for the measurement of CT complexes by use of UV spectroscopy for all the donor-acceptor pairs. Table 1 summarizes the results of the experiments.



The K-values of maleic anhydride derivatives exhibit a reasonable trend which is consistent with the inductive effect of the substituents: the more electron deficient double bond makes a better electron acceptor in CT complexation with DVE. CPD and DMTHNQ, which are similar to MA except for a $-\text{CH}_2-$ group or a $-\text{CH}-\text{CH}-$ group, respectively, in the place of oxygen in MA, have slightly higher K-values than MA because of the two pairs of nonbonding electrons on oxygen in the MA molecule. The larger K-value of the CPD-DVE pair compared to the DMTHNQ-DVE pair is also consistent with the difference in the inductive effect of these groups.

It is seen that there is a parallel relation between the magnitude of the K-values and the cyclocopolymerization behavior: when K is large, a 1:1 cyclocopolymer is obtained with DVE. CPD and MA seem to be on the border in terms of K-values. Although MA does not homopolymerize because of great stability of the MA radical, MA is fairly reactive toward a radical. For example, the methyl affinity is 388, which is relatively large [10]. The methyl group of CA may give more radical stability than MA because of possible

TABLE 1. The Equilibrium Constants of CT Complexation of DVE with Acceptor Monoolefins and Copolymer Composition of Their Cyclocopolymers as Determined by UV. Solvent: CHCl_3 at 25°C .

Acceptor monoolefins ^a	$K \times 10^3$	$\epsilon \times 10^{-2}$	λ_{max} (m μ)	Mole ratio of donor:acceptor in copolymer
DMMA				1:1
CA	3.2	20	<265	1:2
MA	3.6 [4c]	-	278	1:2 [2]
BMA	10.3	10	295	1:1
ChMA	15	5.6	299	1:1
DCMA				1:1 [12]
CPD	7.9	7.7	277	1:1 [6]
DMTHNQ [7]	5.5	11	<265	1:1
THNQ				1:1
FN	0.8 [4c]			1:2 [3]

^aDMMA = dimethylmaleic anhydride; CA = citraconic anhydride; MA = maleic anhydride; BMA = bromomaleic anhydride; ChMA = chloromaleic anhydride; DCMA = dichloromaleic anhydride; CPD = 2-cyclopentene-1,4-dione; DMTHNQ = dimethyltetrahydronaphthoquinone; THNQ = tetrahydronaphthoquinone; and FN = fumaronitrile.

hyperconjugation of the methyl group. Therefore, it is possible that, since K-values are small, reactive free MA and CA "copolymerized" with their respective CT complexes to produce 1:2 alternating cyclocopolymer. (The DVE-FN pair may be in the same category.) The case of the DMMA-DVE pair was a beautiful example of steric effect. Although the K-value of DMMA may be the smallest among the anhydride acceptors in Table 1, and the radical of DMMA is equally as stable as the radical of CA, the cyclocopolymerization with DVE produced only 1:1 cyclocopolymer. It is apparent that the two methyl groups on the double bond sterically prevented the reaction of DMMA toward a cyclized radical of DVE. A tetrasubstituted ethylenic group is generally considered to be sterically unreactive in radical polymerization. As is seen in Table 3, the copolymerization of the DMMA-DVE pair proceeded extremely slowly. The stronger CT complexes of ChMA, BMA, and CPD may

have "homopolymerized" to produce 1:1 cyclocopolymers, and the bulky, free DMMA, DMTHNQ, and THNQ, respectively, did not "copolymerize" with their respective CT complexes, and the 1:1 cyclocopolymers were formed through the "homopolymerization" of the CT complexes. Both the strength of CT complexation and the steric hindrance may play roles in the case of DCMA to give 1:1 cyclocopolymer with DVE.

Figures 1 and 3 show UV absorptions of the CT complexes. The Scott plots are shown in Figs. 2, 4, 5, and 6. The stoichiometry

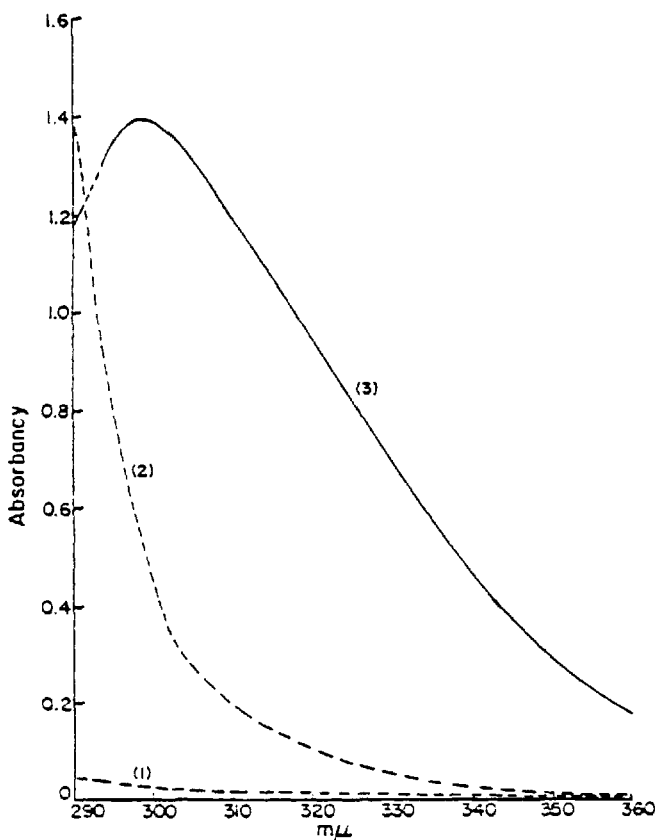


FIG. 1. Absorption of CT complex of ChMA-DVE pair in CHCl_3 at 24°C , path length = 1.0 cm. (1) [DVE], 2.76 moles/liter, sample cell only; (2) [ChMA], 5.78×10^{-3} mole/liter, sample cell only; and (3) [ChMA], 5.78×10^{-3} mole/liter, both sample cell and reference cell; [DVE], 2.76 moles/liter, sample cell only.

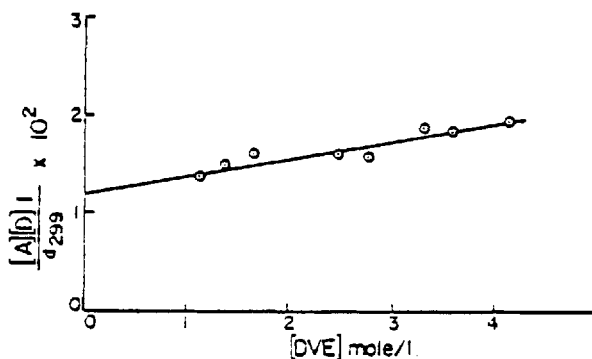


FIG. 2. Scott plot of ChMA-DVE complex in CHCl_3 at 24°C at 299 $\text{m}\mu$. $K = 1.5 \times 10^{-1}$, $E = 5.6 \times 10^2$, and $[\text{ChMA}] = 5.78 \times 10^{-4}$ mole/liter.

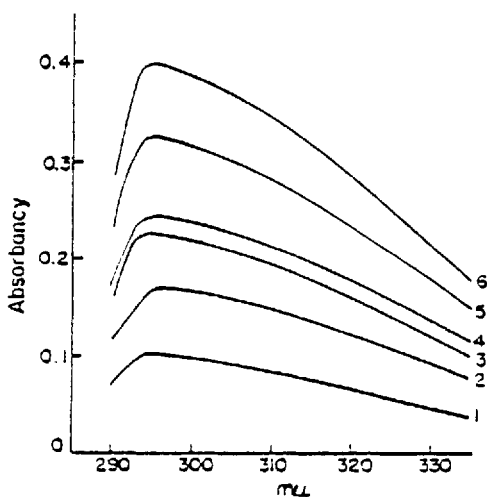


FIG. 3. UV absorption of BMA-DVE CT complex in CHCl_3 at 24°C . $[\text{BMA}] = 9.65 \times 10^{-4}$ mole/liter, (1)-(6): $[\text{DVE}]$, mole/liter, = 1.10 (1), 2.27 (2), 2.77 (3), 3.31 (4), 4.42 (5), and 5.52 (6).

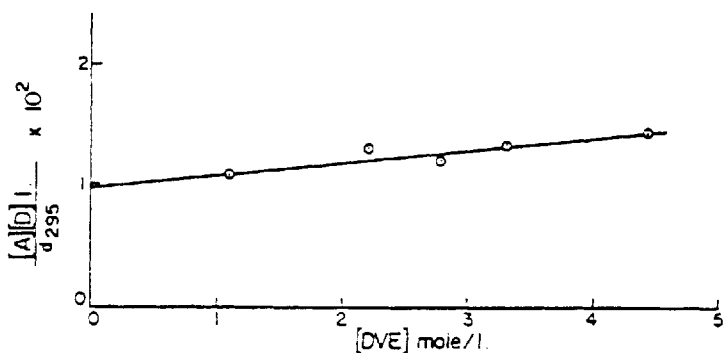


FIG. 4. Scott plot of BMA-DVE complex in CHCl_3 at 24°C at $295\text{ m}\mu$. $[\text{BMA}] = 9.65 \times 10^{-4}$ mole/liter, $K \approx 1.03 \times 10^{-1}$, and $\epsilon \approx 1.0 \times 10^3$.

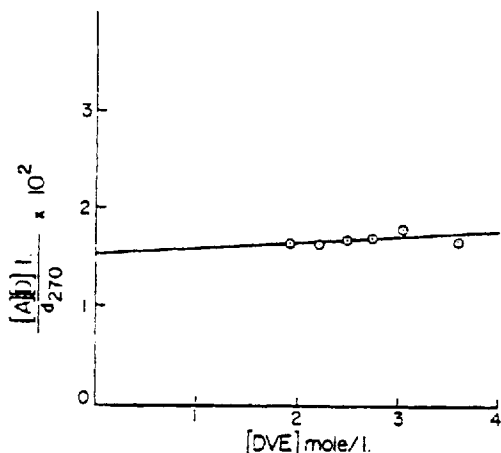


FIG. 5. Scott plot of CA-DVE complex in CHCl_3 at 24°C at $270\text{ m}\mu$. $K = 3.2 \times 10^{-2}$, $E = 2.0 \times 10^3$, and $[\text{CA}] = 1.37 \times 10^{-3}$ mole/liter.

of the CPD-DVE CT complex was determined to be 1:1 in CHCl_3 as shown in Fig. 7.

Elimination of Hydrogen Halide by NaOH and the Structure of the Cyclocopolymer

Facile elimination of HCl by alkalies from cyclocopolymers has been reported. A very facile elimination of hydrogen halides by a

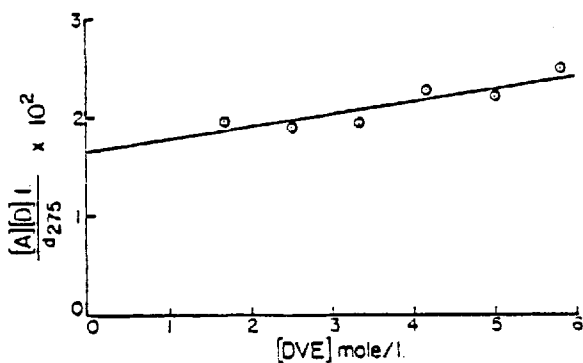


FIG. 6. Scott plot of CPD-DVE complex in CHCl_3 at 24°C at 275 $\mu\mu$. $[\text{CPD}] = 1.042 \times 10^{-3}$ mole/liter, $K \approx 7.9 \times 10^{-2}$, and $\epsilon \approx 7.7 \times 10^2$.

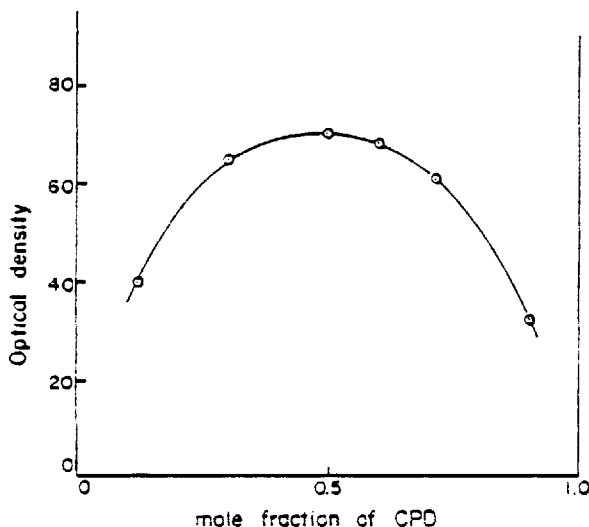


FIG. 7. UV determination of stoichiometric composition of the CT complex of DVE with CPD in CHCl_3 , [6].

very dilute aqueous NaOH solution (0.05 N) was also noted in the present experiments. Thus the cyclocopolymers of ChMA-DVE and BMA-DVE underwent complete elimination of HCl and HBr, respectively, at about 50°C in a few minutes. However, the cyclocopolymer

of DCMA-DVE lost only half the chlorines in the polymer as HCl. The results are summarized in Table 2. The elimination was followed by back-titration with HCl by use of high frequency oscillometry. Typical titration curves are shown in Figs. 8 and 9. The apparent end point of added NaOH appeared earlier by the amount of eliminated hydrogen halides from the copolymers.

TABLE 2. Elimination of Hydrogen Halides by NaOH^a

Cyclocopolymer	Copolymer composition [DVE]/[acceptor]	[HX eliminated] /[acceptor]
ChMA-DVE	1:1	1.0
BMA-DVE	1:1	1.0
DCMA-DVE	1:1	1.0

^a[NaOH] = 0.05 N; reaction temperature = ~50°C; reaction time = ~20 min.

The repeating unit of the cyclocopolymers has been proposed to have six-membered rings resulting from the intramolecular cyclization of a 1,4-diene and a monoolefin [13].

Although the mechanism of the elimination reaction is open to question when the acidity of the eliminated hydrogen is considered, it seems that the elimination of hydrogen halides from ChMA-DVE and BMA-DVE cyclocopolymers follow the reaction Path a, and that of DCMA-DVE cyclocopolymer follows Path b. DCMA-DVE cyclocopolymer underwent elimination of only 1 mole of HCl per mole of DCMA unit. The failure to eliminate a second mole of HCl may be because the incipient negative charge on C₂ is destabilized by the oxygen at Position 3. (The anionic polymerization of vinyl ethers is known to be extremely difficult.) The quantitative elimination of only half the chlorine content of DCMA-DVE cyclocopolymer provides the first support for the proposed six-membered cyclic repeating unit (IX), because there would have been no such elimination if the repeating cyclic unit were five-membered as in (XIII) because the hydrogens to be eliminated would both be at α -position to the oxygen. Also, the product would be a furan derivative which would possess considerable aromatic stabilization.

No vinyl absorptions were detected in the IR and NMR spectra of the cyclocopolymers. NMR showed the following broad peaks: at

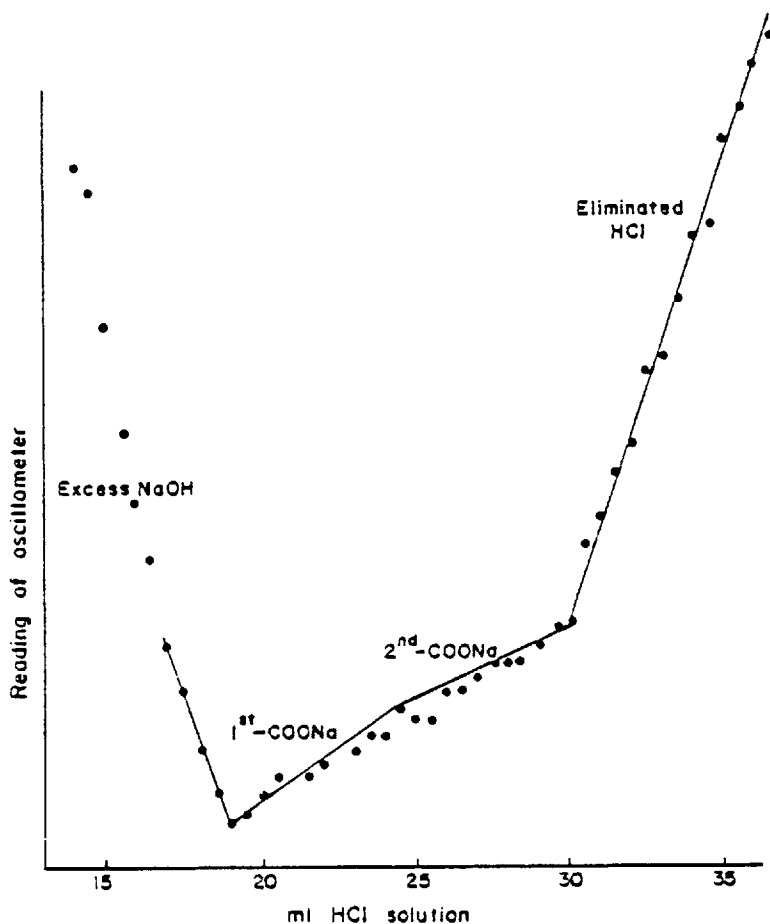


FIG. 8. Titration curve by high-frequency oscillometer. Sample: ChMA-DVE-3. Amount of sample: 62.3 mg. Concentration of HCl solution: 5.57×10^{-2} mole/liter. End point of added NaOH: 36.0 ml HCl solution.

2.36 (α -hydrogens to ether oxygen), at 4.46 (β -hydrogens to ether oxygen) and at 7.36 (hydrogen of ChMA unit in the ChMA-DVE copolymer).

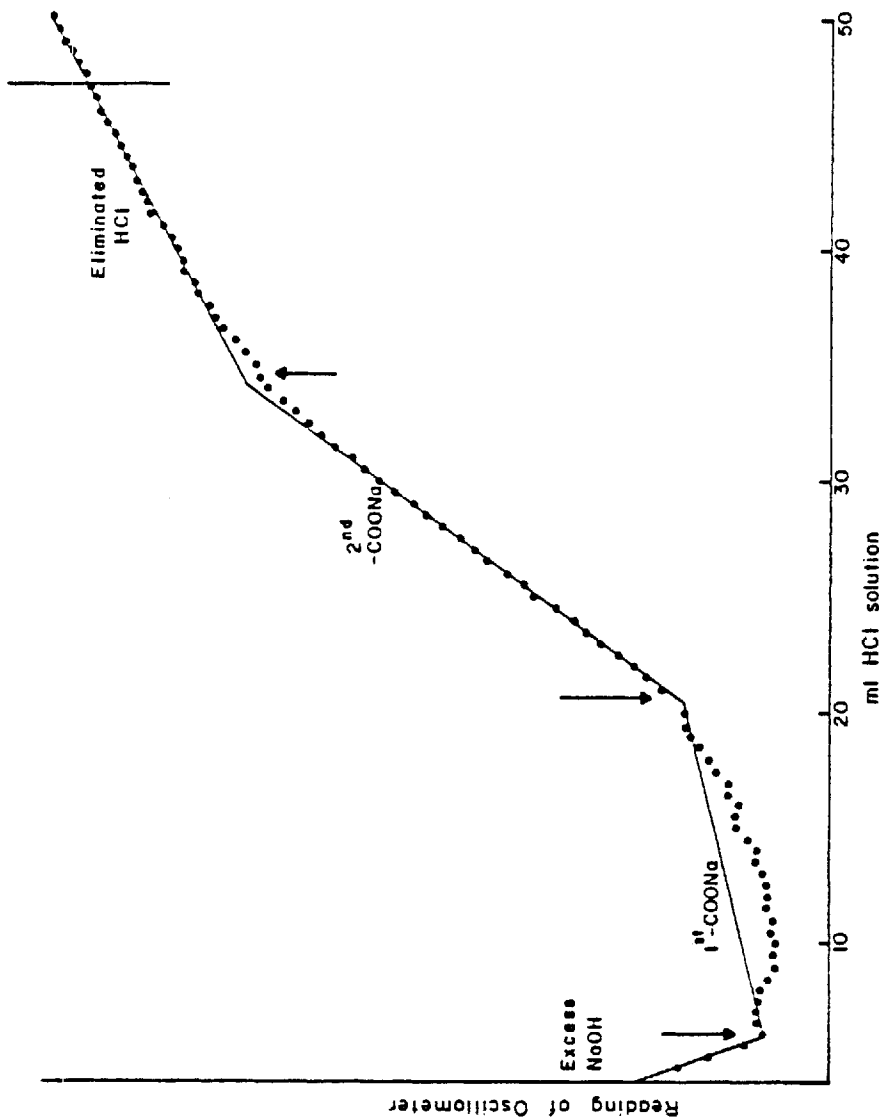
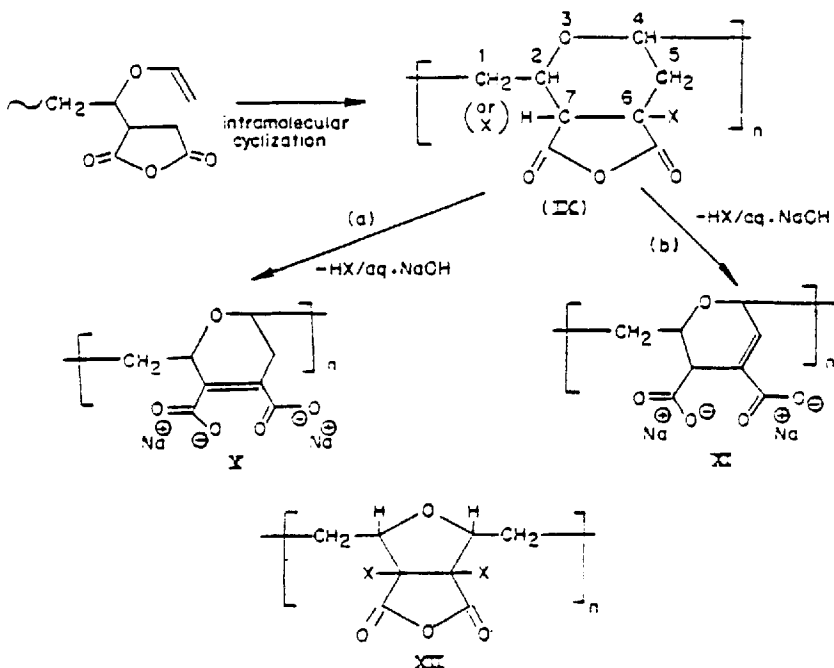


FIG. 9. Oscillometric back-titration of DCMA-DVE cyclocopolymer DCMA-25, 179.8 mg, $[\text{HCl}] = 0.0570 \text{ N}$.



Cyclocopolymerizations

The cyclocopolymerizations of DVE with acceptor monoolefins are summarized in Tables 3, 4, 5, 6, 7, and 8. The copolymer composition curves are shown in Figs. 10 and 11. The copolymer compositions were determined by oscillometric titration of the anhydride groups in the copolymers except for the DCMA-DVE copolymer, the composition of which was determined by chlorine

TABLE 3. Cyclocopolymerization of DMMA-DVE Pair^a

Run No.	Mole fraction of DMMA in feed	Total volume (ml)	Reaction time (hr)	Yield of DMMA in (mg) copolymer	Mole fraction of DMMA in copolymer
DMMA-33	0.333	24	12	27	0.49
DMMA-66	0.666	24	22	38	0.50

^a[DMMA + DVE] = 1.0 mole/liter; [AIBN] = 1.52×10^{-2} mole/liter in $CHCl_3$, at $60^\circ C$.

TABLE 4. Cyclocopolymerization of the CA-DVE Pair at 60°C

Run No.	Mole fraction of CA in feed	DVE (ml)	CA (ml)	Acetone (ml)	AIBN (mg)	Reaction time (min)	Yield (mg)	Mole fraction of CA in copolymer
CA-6	0.197	2.0	0.5	10	60	50	362	0.558
CA-2	0.371	2.5	1.5	5	60	25	^a	0.637 ^b
CA-5	0.497	2.0	2.0	10	60	150	1418	0.664
CA-4	0.795	0.5	2.0	10	60	150	300	0.669 ^c

^aCross-linked^bComposition was measured for soluble portion.^c%C found, 56.13 (calculated 57.2); %H found, 4.63 (calculated 4.77).TABLE 5. Cyclocopolymerization of the BMA-DVE Pair^a

Run No.	Mole fraction of BMA in feed	Total volume (ml)	Reaction time (min)	Yield (mg)	Mole fraction of BMA in copolymer
BMA-25	0.250	16.0	90	123	0.42
BMA-50	0.500	16.0	150	113	0.50

^a [BMA + DVE] = 1.0 mole/liter; [AIBN] = 2.0×10^{-2} mole/liter in acetone at 60°C.

TABLE 6. Cyclocopolymerization of the ChMA-DVE Pair at 60°C

Run No.	Mole fraction of ChMA in feed	DVE (ml)	ChMA (ml)	Acetone (ml)	AIBN (mg)	Reaction time (min)	Yield (mg)	Mole fraction of ChMA in copolymer
ChMA-1	0.250	3.0	1.0	5	60	37	a	0.438 ^b
ChMA-4	0.375	2.5	1.5	5	60	25	750	0.501
ChMA-3	0.750	1.0	3.0	5	60	30	585	0.508 ^c

^aCross-linked.

^bComposition was measured for soluble portion.

^c%Cl found, 16.94 (mole fraction of ChMA by %Cl = 0.487).

TABLE 7. Cyclocopolymerization of the DCMA-DVE Pair^a

Run No.	Mole fraction of DCMA in feed	Total volume (ml)	Reaction time (min)	Yield (mg)	Cl (%)	Mole fraction of DCMA in copolymer ^b
DCMA-25	0.250	16.0	270	423	29.5	0.488 ^c
DCMA-50	0.500	16.0	270	142	29.6	0.489

^a[DCMA + DVE] = 1.325 mole/liter; [AIBN] = 2.28×10^{-2} mole/liter in acetone at 60°C.

^bCopolymer composition was calculated from %Cl.

^cBy titration, mole fraction of DCMA in copolymer was 0.512.

TABLE 8. Cyclocopolymerization of the CPD-DVE Pair [6]^a

Run No.	Mole fraction of CPD in feed	Total volume (ml)	Reaction time (min)	Yield (mg)	Mole fraction of CPD in copolymer
CPD-1	0.100	20	123	361	0.40
CPD-15	0.150	20	25	76	0.45
CPD-25	0.250	20	74	228	0.45
CPD-3	0.300	20	121	366	0.49
CPD-35	0.350	20	45	75	0.45
CPD-55	0.550	20	122	316	0.52
CPD-7	0.700	20	121	123	
CPD-80	0.800	20	200	113	0.46
CPD-9	0.900	20	121	36	0.51

^a[CPD + DVE] = 1.28 mole/liter; [AIBN] = 6.10×10^{-2} mole/liter in DMF at 60°C.

analysis. In all the cases almost constant copolymer compositions were obtained.

EXPERIMENTAL

DVE (Merck, Sharp and Dohme) was distilled before use. Reagent grade DMMA, DCMA, and BMA were purchased from Aldrich Chemical Co., Inc. and were used as received. CA and ChMA were purchased from Aldrich Chemical Co., Inc. and K & K Laboratories, Inc., respectively, and distilled before use. CPD was recrystallized from petroleum ether.

The UV spectra of the CT complexes were taken by using a Beckman DK-2A spectrophotometer in CHCl_3 at 24°C. The equilibrium constants of complexation were calculated by use of the Scott equation [11].

Copolymerization of DVE-acceptor pairs were carried out with α, α' -azobisisobutyronitrile (AIBN) in acetone, CHCl_3 , and N,N-dimethyl formamide (DMF) at $60 \pm 0.02^\circ\text{C}$ in sealed glass tubes. The reaction mixture in the tube was degassed by repeated freeze-and-thaw cycles with liquid nitrogen under a high vacuum before the reaction.

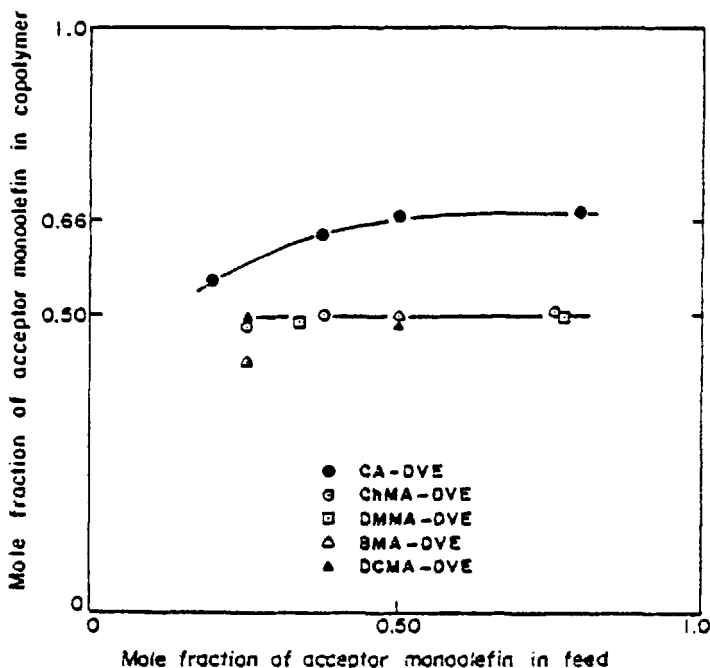


FIG. 10. Mole fraction of acceptor monoolefin in feed. Copolymer composition of cyclocopolymers of DVE with anhydride monoolefins.

The copolymers were separated and purified by repeatedly precipitating from acetone solutions into dry diethyl ether. The copolymers were then dried under vacuum at 50°C before analyses. Copolymers were soluble in acetone (except the CPD-DVE copolymer) and in DMF. The DMMA-DVE copolymer was soluble in CHCl_2 . The CPD-DVE copolymer was purified by precipitating from DMF solution into CCl_4 .

Copolymer compositions of the copolymers of anhydride monoolefins were determined by back-titration of the anhydride units using 0.05 N NaOH and 0.05 N HCl aqueous solutions. The composition of the DCMA-DVE copolymer [12] was calculated from the chlorine content of the polymer. The composition of the CPD-DVE was determined by directly titrating the acidic hydrogen of the CPD unit with 0.05 N sodium methoxide in DMF-methanol mixed solvent. A Sergeant chemical oscillometer, Model V, was used for the titrations.

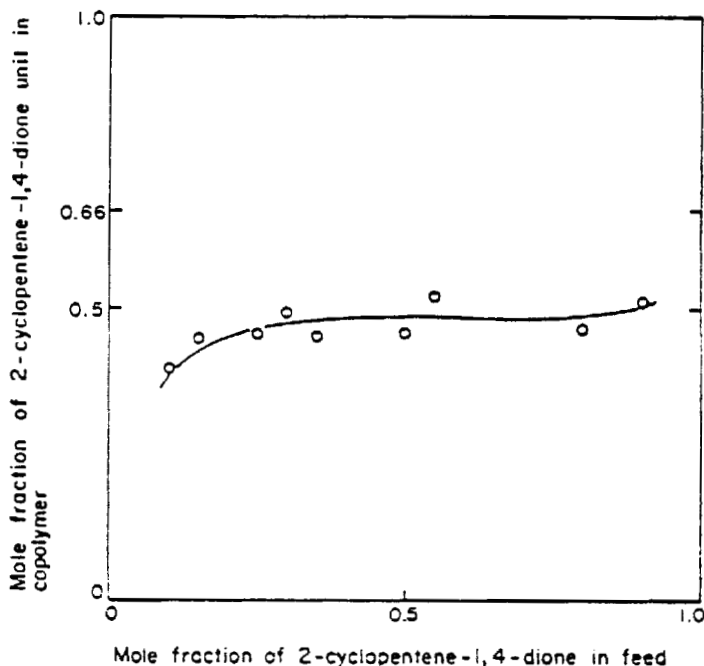


FIG. 11. Composition of DVE-CPD copolymer.

Elemental analyses were done by PCR, Inc., Gainesville, Florida.

Varian Associates analytical NMR, Model A-60, and Beckman IR-10 and IR-8 infrared spectrophotometers were used for characterization of the copolymers. Deuterated acetone was used as solvent for the NMR study. The characteristic IR absorptions, which were taken from KBr pellets, were five-membered anhydride absorption at 1780 and 1860 cm^{-1} , and cyclic ether absorption at 1070 cm^{-1} .

ACKNOWLEDGMENT

This work was supported by the National Institute of Health under Grant No. NIH CA06838, for which we are grateful.

REFERENCES

- [1] T. Kokubo, S. Iwatsuki, and Y. Yamashita, Macromolecules, **1**, 432 (1968).

- [2] J. M. Barton, G. B. Butler, and E. C. Chapin, J. Polym. Sci., Part A, **3**, 501 (1965).
- [3] G. B. Butler, G. Vanhaeren, and M. F. Ramadier, J. Polym. Sci., Part A-1, **5**, 1265 (1967).
- [4] (a) G. B. Butler and K. C. Joyce, J. Polym. Sci., Part C, **22**, 45 (1968). (b) G. B. Butler and A. F. Campus, J. Polym. Sci., Part A-1, **8**, 523 (1970). (c) G. B. Butler and A. F. Campus, J. Polym. Sci., Part A-1, **8**, 545 (1970). (d) G. B. Butler and K. Fujimori, To Be Published in J. Macromol. Sci.—Chem.
- [5] G. B. Butler, G. C. Corfield, and C. Aso, "Cyclopolymerization," in Progress in Polymer Science, Vol. 4 (A. D. Jenkins, ed.), Pergamon, New York, To Be Published.
- [6] K. Fujimori. Master's Thesis, University of Florida. 1968.
- [7] K. Fujimori and G. B. Butler, Joint SE-SW Regional American Chemical Society Meeting, New Orleans, Louisiana, December 1970, Abstracts No. 623; J. Macromol. Sci.—Chem., **A6**, 1609 (1972).
- [8] L. J. Guilbault and G. B. Butler, J. Macromol. Sci.—Chem., **A5**, 1219 (1971).
- [9] K. Fujimori and G. B. Butler, Florida American Chemical Society Meeting-in-Miniature, Gainesville, Florida, May 1971, Abstract B-7; J. Macromol. Sci.—Chem., **A7**, 387 (1973).
- [10] R. W. Lenz, Organic Chemistry of Synthetic High Polymers, Wiley (Interscience), New York, 1967, p. 235.
- [11] R. L. Scott, Rec. Trav. Chem. Pays-Bas, **75**, 787 (1956).
- [12] A. J. Sharpe, Jr., Ph.D. Dissertation, University of Florida, 1970.
- [13] G. B. Butler, Paper Presented at 133rd Meeting of the American Chemical Society, San Francisco, California, April 1958, Abstracts of Papers, p. 6R; J. Polym. Sci., **48**, 279 (1960).

Accepted by editor April 21, 1972

Received for publication June 22, 1972