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### Copolymerization Studies of Cyclopropenone Ketals

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## **Copolymerization Studies of Cyclopropenone Ketals**

GREGORY A. COOK and GEORGE B. BUTLER

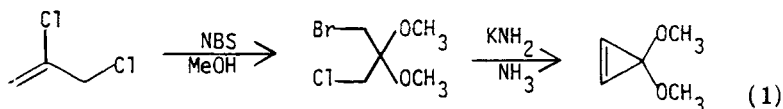
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### **ABSTRACT**

Cyclopropenone ketals have been shown to undergo radical-initiated copolymerization with several conventional comonomers, and their corresponding reactivity ratios were calculated. Low reactivity ratios were obtained and were attributed to steric inhibition of propagation. The structure of the copolymers was elucidated through spectral analysis and chemical modification. Participation of a charge-transfer complex was suggested in the copolymerization of 6,6-dimethyl-4,8-dioxaspiro(2.5)oct-1-ene and N-vinylpyrrolidone. The complex was detected in the UV spectrum, and the equilibrium constant for complexation was determined by NMR techniques. Copolymerization between a 1:1 charge-transfer complex and nonassociated acceptor was proposed to account for a 2:1 incorporation of acceptor to donor in the copolymer.

## INTRODUCTION

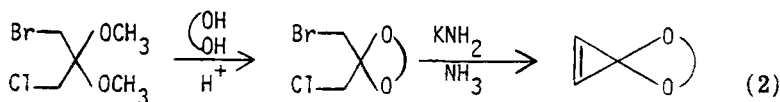
While attempting to synthesize compounds potentially capable of intramolecular charge-transfer complexation, a relatively simple procedure for the preparation of 3,3-dimethoxycyclopropene was developed [1] (Eq. 1). The synthesis involves the treatment of the commercially available 2,3-dichloropropene with N-bromosuccinimide, methanol, and acid catalyst to give 1-bromo-3-chloro-2,2-dimethoxypropane in moderate yields. Subsequent dehydrohalogenation with two equivalents of potassium amide affords the cyclopropenone ketal in 50% yield.



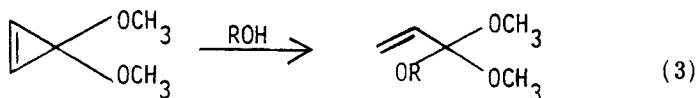
Further investigations of the reactivity of 3,3-dimethoxycyclopropene revealed it to possess an electron-deficient double bond [1, 2]. Diels-Alder reactions of the ketal with several electron-rich dienes gave the corresponding 7,7-dimethoxy-3-norcaradienes in high yields [2]. A Diels-Alder adduct with the electron-rich 1,3-diphenylisobenzofuran was also prepared [1].

Nucleophilic attack at the electron-deficient double bond of 3,3-dimethoxycyclopropene by secondary amines gave rise to a mixture of cyclopropylamines and  $\beta$ -alanine derivatives [2]. Further support for the existence of an electron-poor double bond in 3,3-dimethoxycyclopropene was provided by charge-transfer complexation studies. Equilibrium constants for complexes formed with styrene and divinyl ether, two electron-rich olefins, were measured using NMR techniques. The magnitude of the constant obtained for the complex with styrene was significant, although comparatively lower than that obtained for the styrene-maleic anhydride complex [2].

In an attempt to synthesize a more stable cyclopropenone ketal, several cyclic ketal analogs were prepared. Treatment of 1-bromo-3-chloro-2,2-dimethoxypropane with an appropriate diol (e.g., 2,2-dimethyl-1,3-propanediol) in the presence of acid catalyst gave the corresponding cyclic ketal in high yield. Subsequent dehydrohalogenation by the established procedure afforded several cyclic cyclopropenone ketals which exhibited enhanced stability over the parent compound [3]:



The reaction of alcohols with cyclopropenone ketals provided the first reported synthesis of the orthoacrylates, a novel class of acrylic esters [1-3]:



Recent papers from these laboratories have reported the results of investigations on the cyclopropenone ketals [4, 5] and the orthoacrylates [6]. This paper reports a copolymerization study of the cyclopropenone ketals that was carried out to further establish their chemical reactivities.

The electron-deficient nature of the double bond of cyclopropenone ketals would suggest that homopolymerization should occur via cationic initiation. Results of such studies revealed that a variety of competing reactions occurred [4]; however, polymers possessing at least three structural units in the chain were obtained by this method [5]. Their electron-deficiency would also suggest that radical-initiated copolymerization with electron-rich olefins should occur, even though earlier studies had shown these compounds to be resistant to radical-initiated homopolymerization [4].

## EXPERIMENTAL

### Equipment and Data

All temperatures are reported uncorrected in degrees centigrade. Melting points were determined in sealed evacuated capillary tubes using a Thomas-Hoover melting point apparatus. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia, and Schwartzkopf Laboratory, New York, New York.

Proton nuclear magnetic resonance spectra were obtained using a Varian A-60 spectrometer. All chemical shifts are reported in parts per million (ppm) relative to the internal reference tetramethylsilane (TMS). Instrument conditions are stated for each analysis.

Infrared analysis was carried out on a Perkin-Elmer 281 spectrophotometer. Spectra of solid samples were obtained from a KBr disk, whereas those of liquids were obtained from a film.

The ultraviolet spectral investigations of charge-transfer complexes were completed using a Beckman Acta V spectrophotometer. Quartz cells with a 1 cm path length were used.

Number-average molecular weights of polymers were determined using a Mechrolab Model 302 or a Wescan Model 233 vapor pressure

osmometer. Measurements were carried out in spectral-grade acetone at 37°C. Benzil was used as the calibration standard.

Anhydrous solvents were obtained using the methods described by Gordon and Ford [7]. Nonsolvents for precipitation of polymers were technical grade and were used without further purification. All other solvents were reagent grade and were used as purchased.

## Monomer Synthesis

### Synthesis of 3,3-Dimethoxycyclopropene (I)

This parent member of the cyclopropenone ketal series was synthesized according to Eq. (1) by previously published procedures [4]. Yield: 66%; mp 69–70°C; literature [1], mp 69.5–70.5°C. The monomer was stabilized with 0.1 mol% of hydroquinone and stored at –78°C.

### Synthesis of 4,8-Dioxaspiro(2.5)oct-1-ene (II)

This monomer was synthesized via Eqs. (1) and (2) by a previously published procedure [3, 4] using 1,3-propanediol as the reactant in Eq. (2). Yield: 42%; bp 32–33°C/0.04 mmHg; literature bp 35–40°C/0.3–0.4 mmHg. The monomer was stabilized with 0.1 mol% of hydroquinone and stored at –78°C until ready for use.

### Synthesis of 6,6-Dimethyl-4,8-dioxaspiro(2.5)oct-1-ene (III)

This monomer was synthesized via Eqs. (1) and (2) by a previously published procedure [3, 4] using 2,2-dimethyl-1,3-propanediol as the reactant in Eq. (2). Yield: 55%; bp 33–40°C/0.01 mmHg; literature [3], bp 40–55°C/0.015 mmHg. The monomer was stabilized with 0.1 mol% of hydroquinone and stored at –78°C.

## Polymerization

### Purification of Monomers and Initiators

The cyclopropenone ketals were stabilized with 0.1 mol% of hydroquinone and stored at –78°C. Prior to use, they were stirred over  $\text{CaH}_2$  (except monomer I) for 6 h at  $10^{-6}$  torr and subjected to two bulb-to-bulb distillations. Styrene (St) was washed with 5% NaOH and dried over  $\text{CaSO}_4$  for 24 h. It was then stirred over  $\text{CaH}_2$  for 24 h in vacuo ( $10^{-6}$  torr), followed by two bulb-to-bulb distillations prior to use. Acrylonitrile (AN), 2-vinylpyridine (2VP), and N-vinylpyrrolidone (NVP) were fractionally distilled and dried over  $\text{CaH}_2$  for 24 h in vacuo ( $10^{-6}$  torr). The monomers were then subjected to one bulb-to-bulb distillation prior to use.

Benzoyl peroxide (BP) was dissolved in a minimum amount of  $\text{CH}_2\text{Cl}_2$  and precipitated into methanol twice. It was then dried in

vacuo and stored at 0°C. Azobisisobutyronitrile (AIBN) was recrystallized from diethyl ether, dried, and stored at 0°C.

Copolymerization of Cyclopropenone Ketals With Styrene (St), 2-Vinylpyridine (2VP), Acrylonitrile (AN), and N-Vinylpyrrolidone (NVP)

All copolymerizations were carried out in tared polymer tubes which were washed with anhydrous diethyl ether and flushed with N<sub>2</sub> prior to use. An accurately measured volume of purified comonomer was pipetted into a polymer tube containing 18 mg (0.5 mol%) of purified benzoyl peroxide. Pure cyclopropenone ketal was stored at -78°C under N<sub>2</sub>, and approximate amounts were transferred via syringe to the polymer tube. The actual weight added was determined by weight difference. Four to five samples were prepared containing various initial monomer feed ratios as listed in Tables 1-3. The contents were degassed three times and sealed in vacuo (10<sup>-6</sup> torr). The reaction vessel and connector were weighed, and the copolymerization mixture was heated at 60 ± 0.1°C until a conversion to copolymer of 10% or less was achieved. In each case the contents were diluted in benzene (5-10 mL) and dripped into petroleum ether (250 mL) to precipitate the copolymer (except in the III/AN system where DMF was used as diluent, and in the V/St system where methanol was used as nonsolvent). The filtered copolymers were dissolved and reprecipitated, and 10-20 mg portions of each copolymer sample were lyophilized from benzene in preparation for elemental analysis.

Hydrolysis of Copolymers

Saponification of the pendant ester moiety in the copolymers of cyclopropenone ketals was achieved by treating 50 mg of copolymer with 10 mL of 0.5 N KOH in n-butanol and 1 mL of toluene and refluxing for 12 h. The excess base was neutralized with 1 N HCl, and the hydrolyzed copolymer was precipitated in methanol. After reprecipitating from benzene into methanol, the copolymer was filtered, washed with methanol and pentane, and dried.

Determination of Charge-Transfer Complex Equilibrium Constants

Both ultraviolet (UV) and NMR techniques were employed to study donor-acceptor complex formation between III and NVP. The equilibrium constant for the complex formation was determined by <sup>1</sup>H-NMR techniques. In the UV study, NVP was stirred over CaH<sub>2</sub> for several days and fractionated at 70°C/0.02 mmHg prior to use. Monomer III was stirred over CaH<sub>2</sub> on the high vacuum line for 1 day and subjected to two trap-to-trap distillations prior to use. Spectral grade CCl<sub>4</sub> was used as solvent without further purification.

A stock solution of 0.75 M acceptor was prepared by dilution of 2.63

TABLE 1. Copolymerization of 3,3-Dimethoxycyclopropene (I),  $M_1$ , and Acrylonitrile (AN),  $M_2$ 

Experiment	Mole fraction $M_1$ in feed, $[M_1]$	Reaction time, h	Conversion, %	Mole fraction $M_1$ in copolymer, $d[M_1]$
St-1-I	0.292	4	3.1	0.201
St-2-I	0.423	5	3.0	0.285
St-3-I	0.507	8	2.1	0.345
St-4-I	0.731	9	1.9	0.526



TABLE 2. Copolymerization of 4,8-Dioxaspiro(2.5)oct-1-ene (II),  $M_1$ , and Styrene (St),  $M_2$ 

Experiment	Mole fraction $M_1$ in feed, $[M_1]$	Reaction time, h	Conversion %	Mole fraction $M_1$ in copolymer, $d[M_1]$
St-1-II	0.294	3	8.2	0.172
St-2-II	0.394	4	6.3	0.238
St-3-II	0.514	5.5	5.1	0.320
St-4-II	0.704	7	2.9	0.475

TABLE 3. Copolymerization of 6,6-Dimethyl-4,8-dioxaspiro(2.5)oct-1-ene (III) ( $M_1$ ) and Acrylonitrile (AN), N-Vinylpyrrolidone (NVP), Styrene (St), and 2-Vinylpyridine (2VP) ( $M_2$ )

Experiment	Mole fraction $M_1$ in feed, $[M_1]$	Reaction time, h	Conversion %	Mole fraction $M_1$ in copolymer, $d[M_1]$
AN-1-III	0.280	2	9.9	-
AN-2-III	0.428	2	14	-
AN-3-III	0.293	0.75	7.4	0.275
AN-4-III	0.522	0.75	6.2	0.636
AN-5-III	0.710	2.5	6.2	0.774
AN-6-III	0.823	3	4.4	0.859
NVP-1-III	0.227	4	2.7	0.498
NVP-2-III	0.261	2	5.4	0.545
NVP-3-III	0.407	11	3.1	0.591
NVP-4-III	0.468	14	4.2	0.623
NVP-5-III	0.543	15	3.6	0.644

NVP-6-III	0.552	21	2.7	0.644
NVP-7-III	0.691	0.5	1.2	0.684
NVP-8-III	0.697	1.25	3.3	0.686
NVP-9-III	0.696	120	12	0.688
NVP-10-III	0.725	21	1.9	0.698
NVP-11-III	0.727	24	1.7	0.705
St-1-III <sup>a</sup>	0.247	5	9.4	0.142
St-2-III <sup>b</sup>	0.363	6	7.7	0.209
St-3-III <sup>c</sup>	0.494	7	5.5	0.298
St-4-III <sup>d</sup>	0.624	8	3.9	0.412
2VP-1-III	0.319	1.5	12	0.160
2VP-2-III	0.428	4	11	0.215
2VP-3-III	0.533	4.5	8.2	0.276
2VP-4-III	0.638	5.5	7.5	0.344

<sup>a</sup> $\overline{M}_w = 24,000$ .<sup>b</sup> $\overline{M}_w = 19,600$ .<sup>c</sup> $\overline{M}_w = 17,000$ .<sup>d</sup> $\overline{M}_w = 11,400$ .

TABLE 4. UV Data for Charge-Transfer Complex of III<sup>a</sup> + NVP

Sample	[D]	$\frac{[D]}{[A]}$	Abs <sup>b</sup>	$\frac{[A]}{\text{Abs}}$	$\frac{1}{[D]}$
CT-1	0	-	0	-	-
CT-2	3.0292	19.70	0.112	1.37	0.3301
CT-3	3.6260	23.58	0.136	1.13	0.2758
CT-4	4.3958	28.59	0.186	0.827	0.2275
CT-5	4.9856	32.42	0.195	0.789	0.2006
CT-6	5.4338	35.34	0.205	0.750	0.1840

<sup>a</sup>[A] = 0.15377 in all solutions.<sup>b</sup>Reference = 0.15377 M acceptor in CCl<sub>4</sub>;  $\lambda_{\text{max}}$  = 706 nm.

g of III to 25 mL with solvent; 2.00 mL aliquots were transferred to each of six 10-mL volumetric flasks. Five of the flasks contained accurately weighed quantities of donor, whereas the sixth contained solvent and acceptor for use as the reference. Dilution with CCl<sub>4</sub> to the mark gave five samples with a constant concentration of acceptor and an increasing concentration of donor. The donor monomer was present in at least a 20:1 molar ratio relative to acceptor. Actual concentrations of the comonomers in each sample are listed in Table 4.

TABLE 5. NMR Data for Complex of III<sup>a</sup> and NVP

Sample	Chemical shift (cps)	[D]	[D]/[A]	$[D]^{-1}$ , M <sup>-1</sup>	$(A_{\text{obs}})^{-1}$ , cps <sup>-1</sup>
CT-1	463.25	0	-	-	-
CT-2	464.25	0.36146	6.49	2.76655	1.000
CT-3	465.50	0.87174	15.66	1.14714	0.4444
CT-4	466.50	1.5869	28.50	0.63015	0.3077
CT-5	468.50	2.3374	41.98	0.42782	0.1905
CT-6	469.50	3.0669	55.08	0.32607	0.1600
CT-7	471.25	3.9640	71.19	0.25227	0.1250

<sup>a</sup>[A] = 0.05568.

The procedure for the  $^1\text{H}$ -NMR analysis was similar to that used in the UV study. Monomers were purified by distillation prior to use and stored under  $\text{N}_2$  at  $-78^\circ\text{C}$ . Spectral-grade carbon tetrachloride (Mallinckrodt) was used as purchased. A stock solution of 0.2784 M acceptor with 1% TMS as standard was prepared, and 2.00 mL aliquots were transferred to each of six 10-mL volumetric flasks containing known quantities of NVP (see Table 5). Dilution with  $\text{CCl}_4$  to the mark gave six samples with a constant concentration of acceptor and an increasing concentration of donor which was also present in large excess (greater than 6:1 molar ratio).

## DISCUSSION OF RESULTS

### Copolymerization Studies

Often, monomers which fail to homopolymerize because of steric factors will undergo copolymerization with a suitable comonomer. Such was the case for the cyclopropenone ketal monomers studies, which copolymerized with acrylonitrile (AN), N-vinylpyrrolidone (NVP), styrene (St), and 2-vinylpyridine (2VP). The reactivity ratios were determined by the usual procedure in which varying monomer feed ratios, in bulk, using 0.5 mol% benzoyl peroxide or AIBN as radical initiator (Tables 1-3), were heated at  $60 \pm 0.1^\circ\text{C}$ . Conversion in all cases was 10% or less. The copolymer composition was determined by elemental analysis, and the data were evaluated using the methods of Joshi and Joshi [8] and Kelen and Tüdös [9]. The results are shown in Table 6, where  $r_1$  refers to the reactivity ratio of the cyclopropenone ketal ( $M_1$ ).

The reactivity ratios for cyclopropenone ketals were all less than unity (except for that obtained with AN), indicating the monomer radical possessed a strong bias toward reaction with the other monomer present in the copolymerization mixture. On the other hand, the reactivity ratios for the corresponding comonomers were greater than one, indicative of a propensity to react with its own monomer. As a result, the copolymers obtained were predominantly composed of the comonomer unit. In the case of low mole feed ratios of cyclopropenone ketal, essentially homopolymers of the comonomer were produced.

### Copolymer Structure

Assignment of the structures of the copolymers was based mainly on IR analysis. All of the copolymers exhibited a relatively strong absorbance at  $1735\text{--}1730\text{ cm}^{-1}$  that was attributed to an ester carbonyl stretch. In addition, four broad bands at 1270, 1155, 1070, and

TABLE 6. Reactivity Ratios for Cyclopropenone Ketals

$M_1$	$M_2$	e Value of comonomer <sup>a</sup>	$r_1$	$r_2$
I	St	-0.80	$0.241 \pm 0.053$	$1.40 \pm 0.045$
II	St	-0.80	$0.248 \pm 0.038$	$1.78 \pm 0.038$
III	St	-0.80	$0.254 \pm 0.061$	$1.84 \pm 0.053$
III	2VP	-0.42	$0.071 \pm 0.011$	$2.08 \pm 0.014$
III	AN	1.23	$1.2 \pm 0.4$	$0.4 \pm 0.3$
III	NVP	-1.62	b	b

<sup>a</sup>Obtained from Ref. 10.<sup>b</sup>Nonlinear data.

1030  $\text{cm}^{-1}$  were generally observed due to a C—O—C stretch of the ester unit and perhaps a ketal unit. Other less prominent absorbances were a methyl C—H stretch at 2960  $\text{cm}^{-1}$ , a methylene C—H stretch at 2870  $\text{cm}^{-1}$ , and a C—H bend at 1470  $\text{cm}^{-1}$ . A distinct band at 1630  $\text{cm}^{-1}$ , corresponding to a C=C double bond stretch, was not clearly visible.

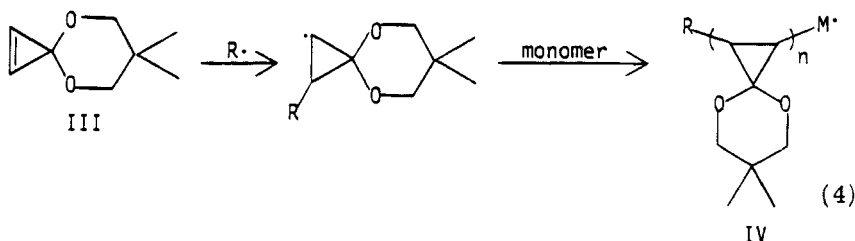
The  $^1\text{H}$ -NMR spectra typically showed a broad absorption at 1.1 ppm ascribed to the gem-dimethyl substituent. Very broad peaks in the regions of 3.3–3.6 ppm and 3.8–4.0 ppm were attributed to methylene protons alpha to ester or ether substituents. No absorption was observed in the region of 5.0–6.0 ppm assigned to olefinic protons. A weak absorption in the region of 0.2–0.5 ppm was detected in copolymer samples containing a high content of cyclopropenone ketal units. On the basis of a chemical shift of 0.2–0.3 ppm reported for the protons of polycyclopropene [11], the absorption was ascribed to the protons of enchaind cyclopropane rings.

Copolymerizations involving 1-methylcyclopropene [12], tetrachlorocyclopropene [13], and tetrafluorocyclopropene [14] have been investigated, and copolymers containing enchaind cyclopropane rings were obtained in all cases. No olefinic absorbances were observed in the NMR or IR spectra of the copolymers prepared, indicating that no isomerization of the cyclopropanyl radical to the stable allyl radical occurred.

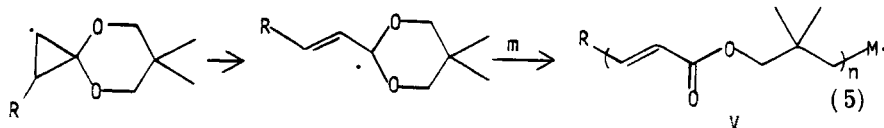
A termination step involving an allylic species, however, was suggested for copolymerizations with tetrachlorocyclopropene [15]. Apparently, some isomerization did occur to form an allyl radical which was too stable to reinitiate polymerization and only participated in combination reactions with other propagating radicals. The presence of a double bond in the copolymer was detected by UV measurements.

According to  $^1\text{H}$ -NMR spectral data, copolymerization of cyclopropenone ketals occurred by radical addition at the double bond to

produce enchaind cyclopropanone ketal repeating units (IV) (Eq. 4). In addition, the presence of cyclopropane rings in the copolymer was indicated by a weak band at  $3020\text{--}3000\text{ cm}^{-1}$  in the IR spectra [12]. (This band was masked by St and 2VP units in these copolymers.)

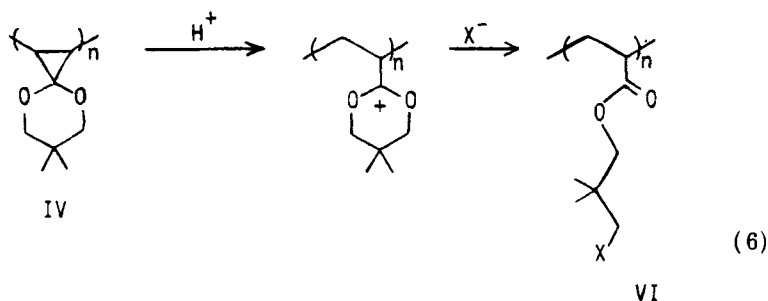


Initially, a mechanism involving isomerization to the allyl radical was proposed to account for the presence of an ester carbonyl band at  $1730\text{ cm}^{-1}$  in the IR spectra (Eq. 5). A similar mechanism was proposed for the  $\text{BF}_3\cdot\text{OEt}_2$  initiated polymerization to account for the acrylate repeating unit (V). However, no spectral evidence for the presence of a double bond was observed for the radical-initiated copolymers.

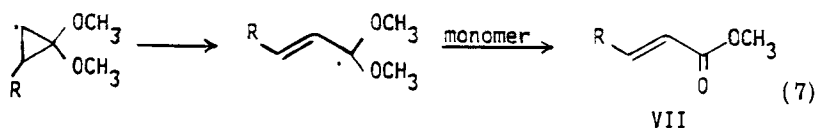


Another possible explanation for the presence of ester groups in the copolymer involves an electrophilic- or radical-induced ring-opening of the cyclopropanone ketal repeating unit (IV) (Eq. 6). Numerous examples have been reported [16] where ring cleavage of cyclopropanone ketals occurred to produce propanoates in the presence of a variety of protonic acids and neutral electrophiles. Also, oxidative cleavage of the cyclopropane ring has been shown to occur in the presence of hydroperoxides [16]. In a similar fashion, adventitious impurities encountered during polymerization or work-up presumably catalyzed ring-opening of the cyclopropanone ketal unit in the copolymer to produce the corresponding propanoate unit (VI).

The absence of any isomerization of cyclopropanyl radicals to allyl radicals in the copolymerization of cyclopropanone ketals was illustrated by copolymerizing I with St. Since I possesses an acyclic ketal moiety, isomerization to the allyl radical and subsequent dealkylation to produce the acrylate unit would have resulted in termination of the propagating chain by formation of VII (Eq. 7). Thus, only cooligomerization would have been expected to occur with high mono-



mer feed ratios of I. Actually, copolymers were obtained with a high content of cyclopropenone ketal units from monomer feeds with a high content of I. As in the case of the cyclic cyclopropenone ketals II and III, the presence of an ester group in the copolymers was apparent, and molecular weights were in the range of 5000-7000.



The presence of propanoate units (VI) in the copolymers of cyclopropenone ketals was illustrated by saponifying the ester moiety with base. Saponification was achieved by refluxing the copolymer in 0.5 N KOH in *n*-butanol. An 80-90% recovery of copolymer comprised of propanoic acid units was obtained. IR analysis revealed the disappearance of the ester carbonyl stretch at  $1730\text{ cm}^{-1}$ , while a COOH stretch at  $3300\text{--}2500\text{ cm}^{-1}$  and a carboxylic acid carbonyl stretch at  $1710\text{ cm}^{-1}$  were observed. Since saponification did not result in chain cleavage of the copolymer, the ester functional groups were determined to be attached to the polymer backbone in accordance with the structural unit (VI) proposed earlier (Eq. 6).

The reactivities of a variety of monomers were correlated by assuming that the rate of propagation ( $k_{22}$ ) of St was constant in all copolymerizations performed under similar conditions. Thus, the reciprocal of the reactivity ratio for St ( $1/r_2$ ) was a measure of the relative reactivities of monomers toward St radicals [17].

In the case of cyclopropenone ketals, monomer II ( $1/r_2 = 0.562$ ) possesses a reactivity similar to monomer III ( $1/r_2 = 0.543$ ) toward St radicals. The similarity in reactivities indicated no steric effect was imparted by the gem-dimethyl substituent on the dioxane ring. This outcome was expected because of the remote distance of the substituent from the reaction center and further supported the proposed mechanism involving propagation of a cyclopropenyl radical



TABLE 7. Summary of  $k_{21}$  Values for Various Monomers

Monomer	Comonomer <sup>a</sup>	$k_{21}$ <sup>b</sup>
Acrylonitrile	Styrene	435
Methyl methacrylate	Styrene	276
Butadiene	Styrene	246
Compound I	Styrene	104
Compound II	Styrene	81
Compound III	Styrene	79
Vinyl chloride	Styrene	8.7
Vinyl acetate	Styrene	2.9

<sup>a</sup> $k_{22} = 145$  for styrene in bulk at 60°C.

<sup>b</sup> $k_{21} = k_{22}/r_2$ .

(Eq. 4). In the case of the mechanism involving ring opening of an allyl radical (Eq. 5), a steric influence imparted by the gem-dimethyl substituents would have been apparent.

Cyclopropenone ketal (I) possesses a substantially smaller ketal substituent compared to those of monomers II and III. As a result, the relative reactivity of I with St radicals ( $1/r_2 = 0.714$ ) is greater than those determined for II and III. The increased reactivity of I reflected a steric effect imparted by the substituents at the C-3 atom of the cyclopropene monomer. Apparently, the bulky dioxane substituents in II and III adversely affected the approach of monomer to the reaction center and ultimately imposed a greater strain on the bonds being formed in the transition state [18].

The rate constant for the reaction of St radical with the cyclopropenone ketal monomer ( $k_{21}$ ) was calculated from the corresponding  $1/r_2$  value and the propagation rate constant for the homopolymerization of St ( $k_{22}$ ) [19]. The values are listed in Table 7, along with the corresponding rate constants of other monomers for comparison.

When the data for the copolymerization of cyclopropenone ketal (III) with NVP were evaluated using the method of Fineman and Ross [20], a nonlinear relationship was obtained. In Fig. 1 the Fineman-Ross plot exhibits two lines with nearly opposite slopes. The intersection of the lines at (-0.768, 1.73) corresponds to an initial monomer feed ratio of 0.499. Thus, when the copolymerization was carried out in excess NVP, incorporation of each monomer proceeded in accordance with the criteria set for the copolymerization equation.

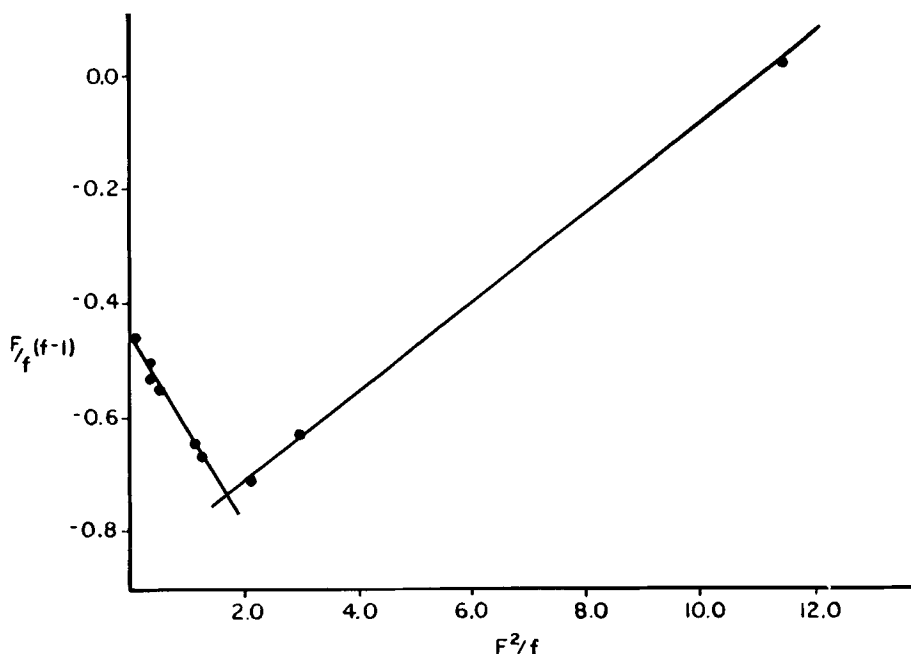


FIG. 1. Fineman-Ross plot for the copolymerization of 6,6-dimethyl-4,8-dioxaspiro(2.5)oct-1-ene (III) and N-vinylpyrrolidone (NVP).

However, in the presence of excess III, a negative slope was obtained (which was not physically meaningful), and one or more of the assumptions of the copolymerization equation had been violated. Since NVP is an extremely strong donor olefin, and III is a weak acceptor monomer, participation of charge-transfer complexation was indicated. In addition, formation of a violet color upon mixing the two monomers provided further evidence for the existence of a charge-transfer complex [21]. Therefore, an investigation of this comonomer pair was carried out with the objectives of detection and measurement of  $K_{eq}$  of the complex using  $^1\text{H-NMR}$  and UV analytical techniques (see Charge-Transfer Complex Studies).

A copolymer composition plot was constructed from the data collected from the copolymerization study of III and NVP by plotting the mole fraction of NVP in the copolymer as a function of its mole fraction in the monomer feed (Fig. 2). The resulting curve is similar to those observed for copolymerization systems where the reactivity ratios of both monomers are less than unity. In such systems there is a definite tendency for each monomer to cross-propagate and form an alter-

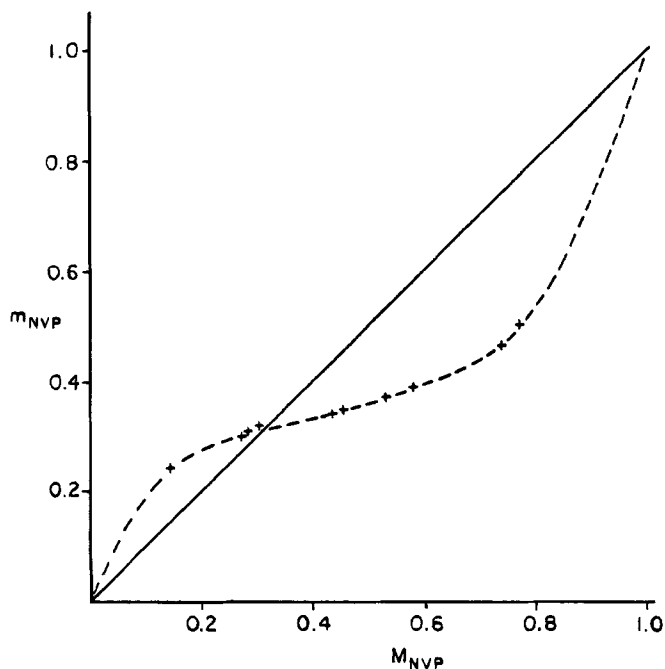
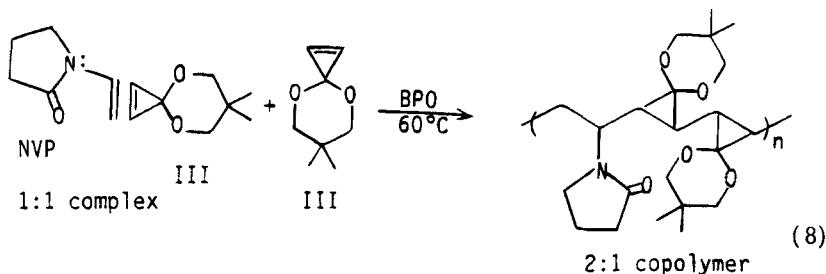


FIG. 2. Copolymer composition plot for the copolymerization of 6,6-dimethyl-4,8-dioxaspiro(2.5)oct-1-ene (III) and N-vinylpyrrolidone (NVP).

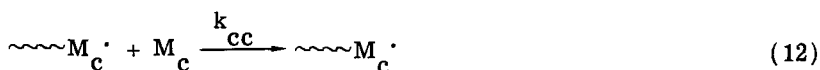
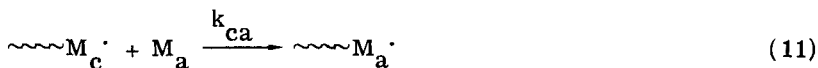
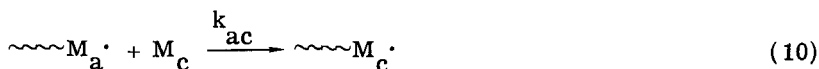
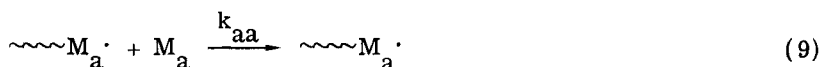
nating copolymer [22]. In addition, an azeotropic copolymerization composition exists at mole fraction  $M_1 = 0.305$  (located at intersection of the curve and diagonal line), where the copolymer composition remained constant throughout the copolymerization.

When the mole fraction of donor monomer (NVP) in the feed was below 0.5, the mole fraction of NVP units in the copolymer was 0.27 to 0.36. In the presence of excess acceptor, therefore, the copolymer composition is essentially a 2:1 ratio of acceptor to donor. Such a composition ratio can be rationalized in two ways: 1) homopolymerization of a charge-transfer complex comprised of two acceptor molecules and one donor molecule, or 2) copolymerization of the 1:1 composition charge-transfer complex with the nonassociated acceptor monomer (Eq. 8). The latter explanation seems more reasonable, since copolymers formed in excess donor monomer approached a 50:50 composition ratio, presumably due to the homopolymerization of the 1:1 complex. Evidently, donor monomer does not copolymerize with the charge-transfer complex, and little or no unassociated acceptor monomer was present to react with the complex. In the case

of a 2:1 composition charge-transfer complex, a 2:1 composition of donor to acceptor in the copolymer would be expected, irrespective of the initial monomer feed ratio.



In order to demonstrate the occurrence of the copolymerization between charge-transfer complex and acceptor olefin, the copolymerization equation was modified to account for complexation. The 1:1 composition charge-transfer complex was treated as an individual monomer, and was denoted  $M_c$ . By assuming 100% complexation, no nonassociated donor olefin was present when the feed contained excess acceptor. Thus, monomer feeds consisting of mole fractions of III greater than 0.5 were comprised of  $M_c$  and nonassociated acceptor monomer which was designated  $M_a$ . By substituting  $M_a$  and  $M_c$  into the classical propagation reactions, four applicable propagation reactions (Eqs. 9-12) were obtained. From these reactions, a modified copolymerization equation (Eq. 13), which defines the copolymerization between  $M_a$  and  $M_c$ , was derived.



$$\frac{d[M_a]}{d[M_c]} = \frac{[M_a]}{[M_c]} \frac{r_a[M_a] + [M_c]}{M_a + r_c[M_c]} \quad (13)$$

where  $r_a = k_{aa}/k_{ac}$  and  $r_c = k_{cc}/k_{ca}$ .

The mole fractions of complex and acceptor present in the monomer feed and the copolymer were determined from the data listed in Table 7 using Eqs. (14) and (15):

$$[M_a] = \frac{[M_1] - [M_2]}{[M_1]} \quad (14)$$

$$d[M_a] = \frac{d[M_1] - d[M_2]}{d[M_1]} \quad (15)$$

Values for the mole fractions are listed in Table 8, along with appropriate data for the calculation of reactivity ratios by the Fineman-Ross method [20]. By plotting  $(F - F/f)$  as a function of  $(F^2/f)$ , a linear relationship was obtained, defined by Eq. (16). A least-squares evaluation of the data gave a slope and intercept corresponding to  $r_a = 0.207$  and  $r_c = 0.0069$ , with a correlation coefficient of 0.991.

$$F = F/f = r_a (F^2/f) - r_c \quad (16)$$

The reactivity ratios of both the complex and the nonassociated acceptor were less than unity, indicating a strong tendency for each radical to cross-propagate. As a result, complex and acceptor olefin were predominantly incorporated into the copolymer in a 1:1 alternating fashion, which ultimately gave rise to a copolymer composed of acceptor (III) and donor (NVP) units in a 2:1 ratio.

#### Q and e Parameters

The Q and e parameters for several cyclopropenone ketals were calculated by solving simultaneous equations (Eqs. 17 and 18) which gave Eqs. (19) and (20). Equation (20) was solved by the quadratic formula, and the resulting  $e_1$  value was substituted in Eq. (19) to obtain the corresponding  $Q_1$  value. Results are listed in Table 9.

$$r_1 = (Q_1/Q_2)e^{-e_1(e_1-e_2)} \quad (17)$$

$$r_2 = (Q_2/Q_1)e^{-e_2(e_2-e_1)} \quad (18)$$

TABLE 8. Data for the Determination of Reactivity Ratios for  $M_a$  and  $M_c$  (Eqs. 14 and 15) for Copolymerization of III and NVP

Experiment	$[M_a]$	$d[M_a]$	$F = \frac{[M_a]}{[M_c]}$	$f = \frac{d[M_a]}{d[M_c]}$	$F - F/f$	$F^2/f$
NVP-5-III	0.158	0.447	0.1876	0.8083	-0.0445	0.0435
NVP-6-III	0.188	0.447	0.2315	0.8083	-0.0549	0.0663
NVP-7-III	0.553	0.538	1.237	1.165	0.175	1.31
NVP-8-III	0.565	0.542	1.299	1.183	0.201	1.43
NVP-9-III	0.563	0.547	1.288	1.208	0.222	1.37
NVP-10-III	0.621	0.567	1.639	1.309	0.387	2.05

TABLE 9.  $Q$  and  $e$  Parameters for Cyclopropenone Ketals and Orthoacrylates

Monomer	$Q_1$	$e_1$	Comonomer	$Q_2^a$	$e_2^a$
I	0.31	0.24	St	1.00	-0.80
II	0.27	0.10	St	1.00	-0.80
III	0.27	0.071	St	1.00	-0.80
III	0.38	0.96	2VP	1.41	-0.42
III	0.4	0.3	AN	0.48	1.23

<sup>a</sup>Values obtained from Ref. 10.

$$Q_1 = (r_1 Q_2) e^{e_1(e_1 - e_2)} \quad (19)$$

$$e_1^2 = 2e_1 e_2 + (e_2^2 + \ln r_1 r_2) = 0 \quad (20)$$

By plotting  $(\ln r_2/Q_2 + e_2^2)$  as a function of  $e_2$ , a straight line was obtained according to Eq. (21). A linear least-squares evaluation of the data gave the  $Q$  and  $e$  parameters (Table 9) with a correlation coefficient of 0.9992.

$$\ln (r_2/Q_2 + e_2^2) = e_1 e_2 - \ln Q_1 \quad (21)$$

The  $Q$  values calculated for the cyclopropenone ketals appeared to correlate well in all of the copolymerization systems. However, the value for parameter  $e$  varied considerably depending on the comonomer used. The variation may be attributed to the inherent deficiencies of the  $Q$ - $e$  scheme mentioned earlier, the lack of sufficiently precise experimental data, or a combination of both.

The positive values for the parameter  $e$  of cyclopropenone ketals are consistent with electron-deficient double bonds in the compounds [2]. Although the monomer is not as strong an acceptor as maleic anhydride ( $e = 3.69$ ) or fumaronitrile ( $e = 2.73$ ), it may form donor-acceptor complexes with sufficiently strong donor olefins, i.e., NVP.

### Charge-Transfer Complex Studies

The ease of nucleophilic addition to the double bond of cyclopropenone ketals has been well documented [1, 2] and is indicative of an electron-deficient olefinic system. Charge-transfer studies on 3,3-dimethoxycyclopropene (I) with two electron-rich monomers, styrene and ethyl vinyl ether, revealed the existence of a weak complex presumably due to electron donor-acceptor interaction [2].

Copolymerization studies of cyclopropenone ketals with various electron-donor olefins, i.e., styrene, 2-vinylpyridine, and N-vinylpyrrolidone (NVP), were undertaken in anticipation of observing the participation of charge-transfer complexes. In most cases, no alternating copolymerization was observed, but rather random copolymers with high compositions of donor monomer were obtained. Apparently, electron donor-acceptor interaction was nonexistent or too weak to effectively influence the copolymerization mechanism. However, the NVP system did exhibit unusual behavior, and participation of a charge-transfer complex was suspected. The complex was faint violet in color and was suspected to be a relatively strong complex. NVP ( $e = -1.62$ ) would be predicted to be a more effective electron-donor than styrene ( $e = -0.80$ ) or 2-vinylpyridine ( $e = -0.42$ ) [10]. Therefore,  $^1\text{H-NMR}$  and UV techniques were employed to detect the existence of a charge-transfer complex and to determine its equilibrium constant.

UV spectroscopy was used to identify a charge-transfer band as an absorption which appeared when the two monomers were mixed. Such a band was observed in the region 720-680 nm, corresponding to the faint-violet color which was produced upon mixing the monomers. This band was not observed in the spectra of pure solvent or pure monomers.

Determination of the equilibrium constant for complex formation was attempted using a procedure similar to that described by Sharpe

[23]. Details concerning sample preparation are outlined in the Experimental Section. Absorbance measurements were carried out on a Beckman Acta V spectrophotometer. The absorbance at the maximum wavelength (706 nm) was measured for each sample with a 0.1538-M solution of acceptor as reference.

Some difficulty was encountered in accurately obtaining absorbance measurements because the magnitude of the absorbance decreased with time. The decrease correlated with a commensurate decrease in the intensity of the violet color of the complex. In order to obtain consistent absorbance readings, samples were examined at exactly  $3 \pm 0.3$  min after mixing the two monomers.

Further complications involving absorbance measurements were caused by an extremely low extinction coefficient for the complex. As a result, high concentrations of comonomers were required in order to obtain measureable absorbances. In addition, the ratio of donor concentration to acceptor concentration was limited to approximately 50:1 by the large volume of donor olefin required.

The data from the UV study (Table 4) were evaluated according to the Benesi-Hildebrand [24] equation (Eq. 22). A plot of  $[A](\text{Abs})^{-1}$  as a function of  $[D]^{-1}$  gave a line with considerable scatter. No attempt was made to derive an equilibrium constant from the available data.

$$[A](\text{Abs})^{-1} = (K\epsilon)^{-1}[D]^{-1} + \epsilon^{-1} \quad (22)$$

An alternative approach to the determination of  $K_{\text{eq}}$  involving  $^1\text{H-NMR}$  techniques was undertaken. Measurement of the equilibrium constant for complexation was achieved by determining the change in chemical shift of the cyclopropenyl protons as a function of donor concentration [25, 26].

The procedure for sample preparation was similar to that employed in the UV study (see Experimental). Comonomer concentrations in each sample were tabulated along with their corresponding chemical shifts (Table 5).

$^1\text{H-NMR}$  measurements were carried out on a Varian A-60 spectrometer at  $38^\circ\text{C}$ . The chemical shift of the cyclopropenyl protons was recorded for each sample and compared with the shift observed for uncomplexed acceptor. By plotting  $(\Delta_{\text{obs}}^A)^{-1}$  as a function of  $[D]^{-1}$ , a straight line was obtained (Fig. 3) according to the linear relationship derived by Hanna and Ashbaugh [27] (Eq. 23).

$$(\Delta_{\text{obs}}^A)^{-1} = (Q\Delta_{\text{AD}}^A)^{-1} + (\Delta_{\text{AD}}^A)^{-1} \quad (23)$$



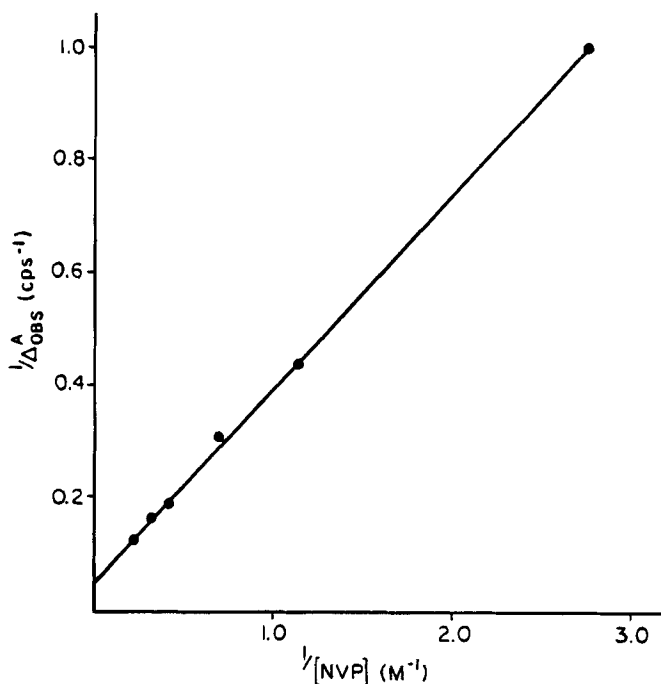


FIG. 3. NMR determination of  $K_{eq}$  for the complex of 6,6-dimethyl-4,8-dioxaspiro(2.5)oct-1-ene (III) and N-vinylpyrrolidone (NVP).

where  $\Delta_{obs}^A$  = the difference between the chemical shift of the acceptor protons in complexed form and that of the acceptor in the uncomplexed form,  $\Delta_{AD}^A$  = the difference in the chemical shift of the acceptor protons in pure complex,  $[D]$  = the concentration of donor monomer, and  $Q = K_{eq}$  for complexation (when  $[D] \gg [A]$ ).

Evaluation of the data by least-squares analysis gave a correlation coefficient of 0.998. The value of  $K_{eq}$  was determined from the slope (see Fig. 3) and  $\Delta_{AD}^A$  was obtained from the intercept, and they are shown in Table 10. Reported values for complexes with I and maleic anhydride (MAN) are shown for comparison.

TABLE 10. Equilibrium Constants of Complexation Determined by NMR

Complex	Solvent	Temperature, °C	K, M <sup>-1</sup>	$\Delta_{AD}^A$ , cps
I:DVE	Hexane	38	0.005	125.0
I:St	CCl <sub>4</sub>	38	0.093	37.0
III:NVP	CCl <sub>4</sub>	38	0.156	18.7
MAn:St [28]	CCl <sub>4</sub>	38	0.216	125.0

## SUMMARY AND CONCLUSIONS

Copolymerization of cyclopropenone ketals with several comonomers was studied, and their corresponding reactivity ratios were calculated. The low reactivity ratios obtained are attributed to steric inhibition encountered during propagation of the 1,2-disubstituted olefin. This steric influence was reflected in the increased relative reactivity of a cyclopropenone ketal monomer bearing a less bulky ketal moiety. Spectral evidence for the presence of enchaind cyclopropenone ketal units was observed. However, considerable ring opening of these units to the corresponding propanoate unit was apparent as indicated by a major ester carbonyl peak in the IR spectra. Hydrolysis of the pendant ester functionality with base was achieved to produce the corresponding propanoic acid unit.

A charge-transfer complex was proposed in the copolymerization of monomers III and NVP. The complex was detected in the UV spectrum, and the equilibrium constant for complexation was determined by NMR techniques. A copolymerization between the 1:1 charge-transfer complex and nonassociated acceptor monomer was postulated to account for a 2:1 incorporation of acceptor to donor in the copolymer. Modification of the copolymerization equation to account for complexation gave a linear relationship when evaluated by the method of Fineman and Ross. The resulting reactivity ratios determined for complex and nonassociated acceptor were less than 0.3, indicating a strong tendency for each radical to cross-propagate.

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