Polymerization and Copolymerization Studies of Orthoacrylates: A Novel Class of Acrylic Esters

Gregory A. Cook[a]; George B. Butler[a]

[a] Center for Macromolecular Science and Engineering and Department of Chemistry, University of Florida, Gainesville, Florida

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GREGORY A. COOK and GEORGE B. BUTLER

Center for Macromolecular Science and Engineering
  and Department of Chemistry
University of Florida
Gainesville, Florida 32611

ABSTRACT

Although ortho-esters constitute a well-known class of organic compounds, the orthoacrylates were unknown prior to a report from these laboratories in 1972. To date, this novel class of acrylic esters has not been investigated as polymerization monomers. We report here polymerization and copolymerization studies of representative members of this class of compounds. Although the orthoacrylates studied did not polymerize in the presence of conventional cationic initiators nor radical initiators, they did respond to radical-initiated copolymerization with a variety of conventional vinyl monomers. Their corresponding reactivity ratios were determined, as well as the Q and e parameters. Monomer syntheses and characterization are reported, as well as structural and properties studies on the copolymers.

INTRODUCTION

The homologous series of compounds known as the orthoacrylates, while obvious members of the well-known orthoester class of organic compounds, was unknown prior to the synthesis of trimethyl ortho-acrylate (I) by Baucom and Butler in 1972 [1]:

(1)

(I)
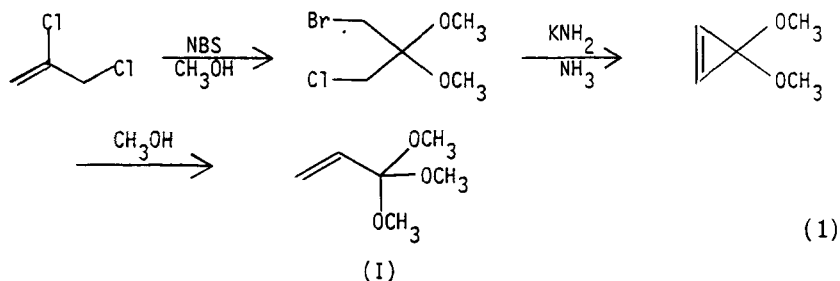
Further investigations were carried out [2, 3] regarding synthesis of a variety of additional members of the homologous series and their characterization; however, no investigations have been directed to-ward studying the polymerization characteristics of this novel class of acrylic esters. It was the purpose of this study to investigate both the homopolymerization and copolymerization characteristics of representative members of this series of acrylate esters. In addition to the method of synthesis reported earlier [1], a novel method of synthesis of these unusual monomers is reported in this paper.

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 spectro-photometer. Spectra of solid samples were obtained from a KBr disk, whereas those of liquids were obtained from a film.

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 [4]. 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. Prepurified nitrogen gas was purchased from Airco, Inc., and was used without further purification.

Synthesis of Monomers and Proposed Intermediates

Preparation of Trimethyl Orthoacrylate (I)

Anhydrous methanol (150 mL) was introduced into a 250 mL round-bottomed flask. The contents were sealed under N_2 with a rubber septum and cooled in an ice-water bath. 3,3-Dimethoxycyclopropene [5] (10 g, 0.10 mol) was injected into the stirred alcohol. The reaction was stirred at 0°C for 3 h and then allowed to warm to 25°C. Methanol was removed in vacuo, and the yellow liquid residue was distilled at 34-36°C/10 mmHg to give 9.8 g of a colorless liquid (74% yield); literature [3], bp 25°C/1 mmHg.

Preparation of 2-Methoxy-2-vinyl-5,5-dimethyl-1,3-dioxane (II) from 6,6-Dimethyl-4,8-dioxaspiro(2.5)oct-1-ene (III)

A 1000-mL three-necked flask equipped with a condenser, $CaCl_2$ drying tube, addition funnel, and N_2 inlet was charged with 400 mL of methanol and approximately 2 g of pulverized CaH_2. The vessel was purged with N_2, and the contents were refluxed for 3 h with stirring. 6,6-Dimethyl-4,8-dioxaspiro(2.5)oct-1-ene (III) (20 g, 0.14 mol) was then added dropwise to the refluxing mixture over a 15-min period. After refluxing for 4 h, the cooled reaction mixture was filtered, and methanol was removed on a rotary evaporator. The faint-yellow liquid residue was fractionally distilled at 36-37°C/1.5 mmHg; literature [3], bp 30°C/1 mmHg. The yield was 17.5 g or 73% of theory.

The NMR spectrum showed two three-proton singlets at 0.79 and 1.15 ppm, a three-proton singlet at 3.21 ppm, a two proton doublet at 3.31 ppm, a two-proton doublet at 3.83 ppm, and a three-proton multiplet at 5.20-5.78 ppm.

Compound II was also prepared via VIII and VII (see below and Eq. 4).

Synthesis of 2-Methoxy-2-vinyl-5,5-dimethyl-1,3-dioxane (II) from 2-Vinyl-5,5-dimethyl-1,3-dioxenium Tetrafluoroborate (VII)

A procedure similar to that described for the synthesis of VI was carried out using the following quantities of starting materials: 1.4 g (6 mmol) of VII, 4 mL of pyridine, and 20 mL of methanol. The yield

of II was 0.91 g or 88% of theory. The NMR spectrum was identical
to that reported for II synthesized from III.

Preparation of Diethoxycarbonium Hexachloroantimonate (IV)

A procedure similar to that described by Meerwein et al. [6] was
employed. A 25-mL round-bottomed flask was charged with 14.9 g
(50 mmol) of antimony pentachloride and 4 mL of anhydrous CH_2Cl_2.
The contents were sealed under N_2 with a rubber septum and cooled
to -30°C. Triethyl orthoformate (3.7 g, 25 mmol) was injected into
the stirred reaction mixture. Colorless crystals of ethoxytetrachloro-
antimonate immediately appeared. The mixture was allowed to stand
for 2 h at -30°C, and then the liquid was filtered from the crystalline
residue. The crystals were washed with 6 mL of cold (-30°C)
CH_2Cl_2, and the combined filtrates were poured into 200 mL of CCl_4
and stored overnight at 0°C. The product was filtered and dried in
vacuo to give 8.0 g (74% yield); mp 150-153°C; literature [6], mp
151-152°C.

Synthesis of Vinyldiethoxycarbonium Hexachloroantimonate (V)

A 25-mL round-bottomed flask was charged with 4.4 g (10 mmol)
of IV and 7 mL of CH_2Cl_2, and the contents were sealed under N_2
with a rubber septum. The mixture was cooled to 0°C, and 1.2 mL
(11 mmol) of ethyl acrylate was injected in one portion. Stirring was
continued for 4 h at 0°C, and then the reaction mixture was poured
into 150 mL of Et_2O. The salt which precipitated was filtered, washed
with Et_2O, and dried in vacuo. The yield of product was 2.8 g or 60%
of theory. The NMR spectrum showed a six-proton triplet at 1.80
ppm, a four-proton quartet at 5.12 ppm, and a three-proton multiplet
at 6.22-7.30 ppm.

Preparation of Diethylmethyl Orthoacrylate (VI)

A 50-mL round-bottomed flask was charged with 4 mL of pyridine
and 20 mL of anhydrous methanol. The contents were sealed under
N_2 with a rubber septum and cooled to -78°C. To the stirred solution
was added 2.8 g (6.0 mmol) of V that was dissolved in 3 mL of CH_2Cl_2,
and the reaction mixture was stirred for 2 h at -78°C. The mixture
was poured into 60 mL of cold CCl_4 and then extracted with 40 mL of
10% aqueous NaOH. The organic layer was dried over $CaCl_2$, and sol-
vent was evaporated. The liquid residue was identified as the desired
orthoacrylate by NMR. The yield was 0.80 g or 83% of theory.
The NMR spectrum showed a six-proton triplet at 1.20 ppm, a
three-proton singlet at 3.24 ppm, a four-proton quartet at 3.47 ppm,
and a three-proton multiplet in the region of 5.3-5.7 ppm. The spec-
trum was identical to that reported in the literature [3].

Preparation of 2-Vinyl-5,5-dimethyl-1,3-dioxenium Tetrafluoro-
borate (VII) and 2-Methoxy-2-vinyl-5,5-dimethyl-1,3-dioxane (II)
from β,β-Dimethyl-γ-bromopropylacrylate (VIII)

In accordance with Eq. (4), both the carbocationic salt (VII) and the
orthoacrylate (II) were prepared as reported earlier [5]. All spectral
data and other properties corresponded to those reported earlier.

Preparation of β,β-Dimethyl-γ-bromopropylacrylate (VIII)

This compound was prepared as described in an earlier publication from this laboratory [5, 7] in accordance with Eq. (4). All spectral data were identical to those reported earlier.

Preparation of 2-Vinyl-5,5-dimethyl-1,3-dioxenium Tetrafluoroborate (VIII) from 2-Methoxy-2-vinyl-5,5-dimethyl-1,3-dioxane (II)

A 25-mL round-bottomed flask was charged with 1.7 g (10 mmol) of 2-methoxy-2-vinyl-5,5-dimethyl-1,3-dioxane (II) and 10 mL of anhydrous diethyl ether. The contents were sealed under N_2 with a rubber septum and cooled to -78°C. To the stirred solution was injected 1.2 mL (10 mmol) of $BF_3 \cdot OEt_2$ dropwise over a 5-min period. After 15 min the ether was decanted from a waxy solid which adhered to the surface of the flask. The solid was taken up in a minimum volume of CH_2Cl_2 and precipitated in ether. After decanting the ether, the solid was again dissolved in CH_2Cl_2 and reprecipitated in ether. The salt was scraped from the flask, filtered under a stream of N_2, washed with ether several times, and transferred under a layer of ether to a 10-mL round-bottomed flask. The white solid was dried on the high vacuum line (10^{-6} torr) overnight to give 0.59 g or a 35% yield based on $BF_3 \cdot OEt_2$. The NMR spectrum was identical to that described earlier for VII [5].

Copolymerization of Orthoacrylates with Styrene (St), Acrylonitrile (AN), and 2-Vinylpyridine (2-VP)

All copolymerizations were carried out in tared polymer tubes which had been washed with anhydrous diethyl ether and flushed with N_2 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 monomer was stirred at -78°C under N_2, 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 Table 1. The contents were degassed three times and sealed in vacuo (10^{-6} 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. 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 orthoacrylates 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

TABLE 1. Copolymerization of Orthoacrylates with Acrylonitrile (AN), Styrene (St), and 2-Vinylpyridine (2VP)

Experiment	Mole fraction M_1 in feed	Reaction time, h	Conversion, %	Mole fraction M_1 in copolymer
$M_1 = I; M_2 = 2VP:$				
VP-1	0.189	1	7.4	0.086
VP-2	0.359	$1\frac{1}{2}$	2.6	0.180
VP-3	0.495	$4\frac{1}{2}$	1.1	0.261
VP-4	0.597	6	1.5	0.314
$M_1 = II; M_2 = AN:$				
AN-1	0.260	3/4	12	0.141
AN-2	0.357	1	10	0.184
AN-3	0.478	$1\frac{1}{2}$	8.1	0.248

|				
$M_1 = II; M_2 = St$:				
St-1[a]	0.250	24	48	–
St-2[b]	0.375	24	38	–
St-3	0.276	2	4.5	0.051
St-4	0.453	2	3.4	0.109
St-5	0.542	$2\frac{1}{2}$	3.0	0.129
St-6	0.714	3	2.6	0.184
St-7	0.824	$3\frac{1}{2}$	2.4	0.305
$M_1 = II; M_2 = 2VP$:				
VP-1	0.416	3/4	8.0	0.061
VP-2	0.456	1	8.0	0.065
VP-3	0.533	5	11	0.079
VP-4	0.679	2	8.7	0.074
VP-5	0.798	$2\frac{1}{2}$	6.4	0.108

[a] $\overline{M}_w$ = 22,800.
[b] $\overline{M}_w$ = 19,500.

copolymer was precipitated into methanol. After reprecipitating from benzene into methanol, the copolymer was filtered, washed with methanol and pentane, and dried.

## RESULTS AND DISCUSSION

Synthesis of Orthoacrylates

The synthesis of 2-methoxy-2-vinyl-5,5-dimethyl-1,3-dioxane (II) was carried out by refluxing methanol over calcium hydride, followed by the dropwise addition of 6,6-dimethyl-4,8-dioxo(2.5)oct-1-ene (III). Orthoacrylates had been prepared previously [1-3] by treating an appropriate cyclopropenone ketal with absolute alcohol that had been distilled from magnesium prior to use. By synthesizing the orthoacrylates in the presence ov CaH_2, the alcohol purification step was eliminated, and the percentage yield of product was increased from 50 to 73%.

$$\tag{2}$$
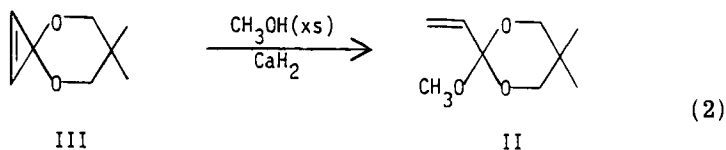
An alternate synthesis of orthoacrylates was also developed which involved nucleophilic addition of an alkoxide anion to vinyl dialkoxycarbonium ion. For example, when ethyl acrylate was treated with diethoxycarbonium hexachloroantimonate (IV), alkylation occurred at the carbonyl oxygen atom to form vinyldiethoxycarbonium hexachloroantimonate (V). The salt was isolated and treated with sodium methoxide to give the corresponding diethylmethyl orthoacrylate (VI) in high yield:


$$\tag{3}$$
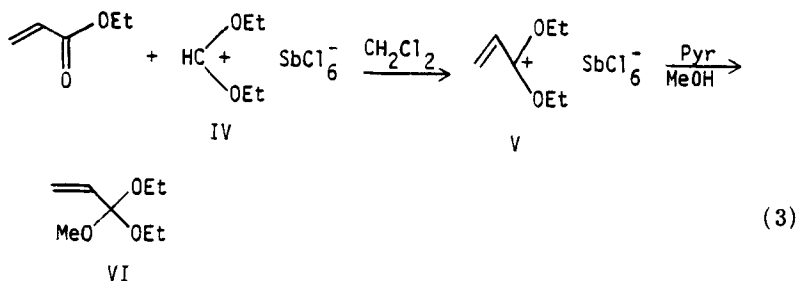
Likewise, 2-vinyl-5,5-dimethyl-1,3-dioxenium tetrafluoroborate (VII) was synthesized by an intramolecular alkylation at the carbonyl oxygen atom when β,β-dimethyl-γ-bromopropylacrylate (VIII) was treated with AgBF$_4$ (Eq. 4). Subsequent nucleophilic addition of methoxide to VII gave the orthoacrylate (II):
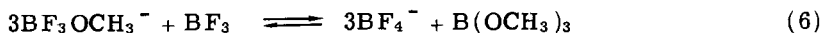

VIII

VII   II   (4)
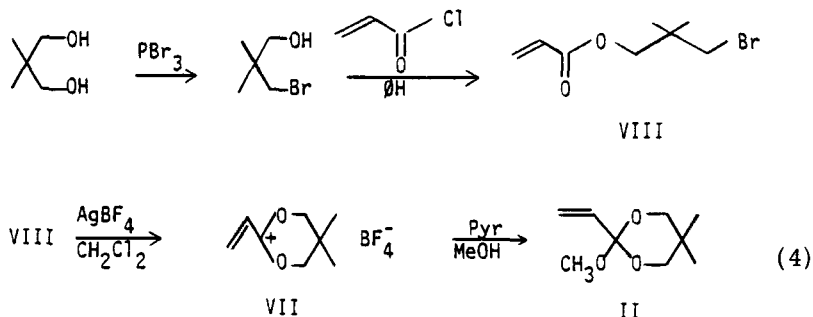
Cationic Initiation of Orthoacrylates

Attempted polymerization of 2-methoxy-2-vinyl-5,5-dimethyl-1,3-dioxane (II) with BF$_3 \cdot$OEt$_2$ under a variety of conditions resulted in no detectable reaction. As in the case of cyclopropenone ketals [5], the concomitant formation of a stable carbocation intermediate was suspected.

In an attempt to isolate a stable cationic intermediate from orthoacrylate monomers, II was treated with one equivalent of BF$_3 \cdot$OEt$_2$ in dry diethyl ether at -78°C. A hygroscopic solid was obtained in 25% yield which exhibited NMR spectral data identical to that of 2-vinyl-5,5-dimethyl-1,3-dioxenium tetrafluoroborate (VII) synthesized earlier [5]. Apparently, BF$_3 \cdot$OEt$_2$, acting as an alkoxide acceptor, abstracted methoxide anion to produce the corresponding dialkoxycarbonium salt (Eq. 5). A similar synthetic route had been employed to prepare a variety of dialkoxycarbonium salts from orthoesters [6].

II   VII
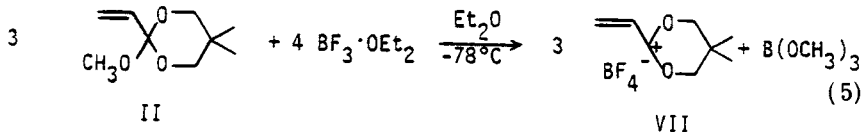
The tetrafluoroborate counterion arose from the disproportionation of methoxytrifluoroborate with boron trifluoride. The greater stability of the tetrafluoroborate anion caused a substantial shift of the equilibrium in favor of BF$_4{}^-$ (Eq. 6) [6]. No methoxy protons were observed in the NMR spectrum of VII.

$$3BF_3OCH_3^- + BF_3 \rightleftharpoons 3BF_4^- + B(OCH_3)_3 \qquad (6)$$

The NMR spectra of the vinyl dialkoxycarbocation (VII) isolated from II and VIII were identical and were also in good agreement with the spectral data reported for 2-vinyl-1,3-dioxolenium tetrafluoroborate (IX) in fluorosulfonic acid medium [8]. In all of the spectra, the vinyl protons and the ether methylene protons were shifted downfield due to the presence of the positive charge [9, 10]. The chemical shifts observed for VII in CD_3CN differed somewhat from those of IX because of the different solvents employed for NMR analysis [11].

When II was treated with 5 mol% of VII, no detectable reaction occurred after 3 h at 25°C. The low reactivity of the carbocation was ascribed to the resonance-derived stabilization of the positive charge discussed earlier [5]. Thus, monomer II did not polymerize in the presence of $BF_3 \cdot OEt_2$ due to the occurrence of a facile alkoxide abstraction to produce a cationic species (VII) which was not sufficiently reactive to sustain propagation.

Radical Initiation

All attempts to homopolymerize orthoacrylates by a radical chain-growth mechanism were unsuccessful. Radical initiators such as azobisisobutyronitrile and benzoyl peroxide in the temperature range of 25-80°C were investigated. The low reactivity of these monomers can be attributed to steric inhibition of propagation by the bulky ortho ester substituent and alkoxide radical abstraction to produce a resonance-stabilized allyl radical intermediate.

Radical-Initiated Copolymerization of Orthoacrylates

In the copolymerization of 2-methoxy-2-vinyl-5,5-dimethyl-1,3-dioxane (II) with several comonomers, essentially homopolymers of the comonomer were produced (Table 1). The corresponding reactivity ratios for the orthoacrylate were zero, indicating the radical exhibited virtually no tendency to react with its own monomer (Table 2). Other monomers which have been shown to behave similarly are 1,1- and 1,2-disubstituted ethylenes [12].

The low reactivity of monomer II is not surprising, since the orthoester functional group is unable to enhance the reactivity of the double bond through resonance or electronic effects. Furthermore, the orthoester moiety is bulky and may have caused steric inhibition of propagation and a decreased enthalpy of polymerization. The enthalpy of polymerization for ethylene is -22.7 kcal/mol. The corresponding enthalpy for the orthoacrylate is expected to be much smaller due to steric strain differences in the monomer and polymer arising from bond angle deformation and bond stretching [13].

Decreased ΔH values are typical of 1,1-disubstituted ethylenes where 1,3-interactions between pendant groups cause a strained polymeric structure [12]. Although the orthoacrylate is not disubstituted,

TABLE 2. Results for Copolymerizations of Orthoacrylates

Orthoacrylate	r_1	Comonomer	r_2	$\dfrac{1}{r_2}$
I	0.17^a	2VP	2.33^a	0.429
II	0	St	6.53 ± 0.02	–
II	0	2VP	8.76 ± 0.08	0.114
II	0	AN	1.77 ± 0.02	–

[a]Determined by the Fineman-Ross method; R = 0.998.

the mono-substituent is sufficiently large to adversely interact with an α-hydrogen atom.

The entropy of polymerization is relatively insensitive to monomer structure and varies within a narrow range of 25-30 cal/°K-mol. Thus, at 60°C the $T\Delta S$ value is a maximum of 9.9 kcal/mol. If the corresponding enthalpy of polymerization is less than -10 kcal/mol (as in the case of α-methylstyrene where $\Delta H = 8.4$ kcal/mol), then polymerization is thermodynamically prohibited [12].

The steric influence of the orthoester substituent on the polymerization of orthoacrylates is illustrated by copolymerizing the less bulky trimethyl orthoacrylate (I) with 2-vinylpyridine. By comparison of $1/r_2$ values, the orthoacrylate (I) was found to be considerably more reactive than II toward 2-vinylpyridine radicals (Table 2).

Some difficulty was encountered in characterizing the orthoacrylate repeating unit by infrared and NMR analysis because of the low content of that monomer unit in the copolymer. In general, the copolymers exhibited a relatively strong ester carbonyl band at 1720 cm^{-1} in the infrared (IR) spectra. Other less prominent absorbances included a methyl C–H stretch at 2950 cm^{-1}, a methylene C–H stretch at 2870 cm^{-1}, and a group of four bands at 1270, 1177, 1062, and 1026 cm^{-1} attributed to an ester C–O–C stretch.

The IR spectral data for the copolymers of II showed the presence of an ester unit, which suggested that the pendant orthoester moiety had undergone hydrolysis during or subsequent to polymerization. The high hydrolytic reactivity of trialkyl orthoesters has been well established in the literature by kinetic studies [14, 15]. Typically, orthoesters are readily hydrolyzed in the presence of small amounts of water by a general acid catalysis mechanism involving the formation of a dialkoxycarbocation intermediate [16]. Thus, the structure of the hydrolyzed orthoacrylate unit was a propanoate repeating unit (X):
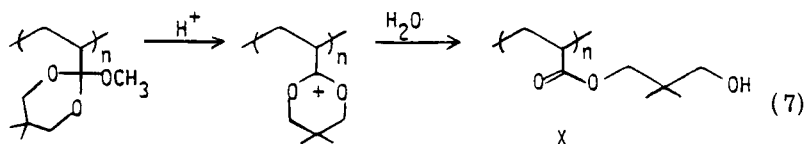
Saponification of the propanoate unit (X) with base gave the corresponding carboxylic acid identified by IR.

Q and e Parameters for Orthoacrylates

The Q and e parameters for trimethyl orthoacrylate (I) were calculated by solving simultaneous Eqs. (8) and (9), which gave Eqs. (10) and (11). Equation (11) was solved by the quadratic formula, and the resulting e_1 value was substituted in Eq. (10) to obtain the corresponding Q_1 value. The results are listed in Table 3.

$$r_1 = (Q_1/Q_2)e^{-e_1(e_1-e_2)} \tag{8}$$

$$r_2 = (Q_2/Q_1)e^{-e_2(e_2-e_1)} \tag{9}$$

$$Q_1 = (r_1Q_2)e^{e_1(e_1-e_2)} \tag{10}$$

$$e_1^2 = 2e_1e_2 + (e_2^2 + \ln r_1r_2) = 0 \tag{11}$$

Since the reactivity ratios of the orthoacrylate monomer (II) were zero, the Q and e parameters were determined using the least-squares method of Schneider [17]. By plotting $(\ln r_2/Q_2 + e_2^2)$ as a function of e_2, a straight line was obtained according to Eq. (12). A linear least-squares evaluation of the data gave the Q and e parameters (Table 3) with a correlation coefficient of 0.9992.

TABLE 3. Q and e Parameters for Orthoacrylates

Monomer	Q_1	e_1	Comonomer	Q_2 [a]	e_2 [a]
I	0.40	0.54	2VP	1.41	-0.42
II	0.19 [b]	0.71 [b]	St 2VP AN	--	--

[a]Values obtained from Ref. 18.
[b]Determined by least squares analysis.

$$\ln \left(r_2 / Q_2 + e_2{}^2 \right) = e_1 e_2 - \ln Q_1 \tag{12}$$

The Q and e values for the two orthoacrylate monomers differed because the Q-e scheme does not take into account steric effects. It is reasonable to assume that the resonance and polar properties of the two monomers are sufficiently similar to expect nearly equivalent Q and e values. Thus, the variation must have been the result of the size differences of the orthoester moiety.

SUMMARY AND CONCLUSIONS

The objectives of this investigation were 1) to improve the existing syntheses and develop new syntheses for the orthoacrylates, 2) to study their polymerizability with a variety of initiator systems, and 3) to copolymerize these monomers to further establish their chemical reactivities. Modifications in the synthesis of the orthoacrylates enhanced the yield and operational convenience of the procedure. In addition, an alternate synthesis of orthoacrylates was devised which did not require a cyclopropenone ketal precursor.

The orthoacrylates did not homopolymerize in the presence of a variety of cationic initiators. In each case the formation of a stable carbocation intermediate was suggested to account for their sluggish reactivity. Synthesis and isolation of these intermediates were achieved by reacting equivalent amounts of monomer and $BF_3 \cdot OEt_2$ at $-78°C$. The resulting cationic intermediates were characterized by NMR, and their low reactivity toward monomer was demonstrated.

Attempts to homopolymerize the orthoacrylates with radical initiators were unsuccessful. Apparently, the orthoester moiety was sufficiently bulky to adversely influence the propagation rate. The inhibitory influence of the substituents on these monomers was further supported in the copolymerization studies.

Copolymerization of orthoacrylates with several comonomers was accomplished. Reactivity ratios were determined which revealed that the radical generated from the orthoacrylate monomer was virtually inert toward like monomer. The low reactivity was attributed to steric prohibition of propagation by the bulky orthoester substituent. The copolymers of orthoacrylates contained propanoate ester units arising from hydrolysis of the orthoester moiety during or subsequent to polymerization.

ACKNOWLEDGMENTS

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