SYNTHESIS AND POLYMERIZATION OF SOME NON-CONJUGATED DIENES

By
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Abstract of Dissertation Presented to the
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Synthesis and Polymerization of Some Non-Conjugated Dienes

By
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December 1974

Chairman: George B. Butler
Major Department: Chemistry

Three isomeric non-conjugated dienes, o-, m-, and p-
(2-vinylxyethoxy)styrenes, were selectively polymerized by
anionic or radical initiators through the styryl double
bond while leaving the vinyl ether moiety intact. The
anionic-initiated polymeric products were of high molecular
weight and narrow molecular weight distribution as charac-
terized by membrane osmometry and gel permeation chromato-
graphy, respectively. These polymers could be subsequently
crosslinked by cationic initiator via the vinyl ether moiety
on the polymer side-chains.

Acid-catalyzed hydrolysis of poly-(2-vinylxyethoxy)-
styrenes yielded their respective hydroxy-containing polymers,
polyvinylphenoxyethanols. The latter were physically and
spectroscopically identical to authentic samples prepared by
radical polymerization of vinylphenoxyethanols, which, in turn, were synthesized by hydrolysis of (2-vinylphenoxyethoxy)-styrenes. The polyvinylphenoxyethanols could undergo many chemical transformations, such as esterification with 3,5-dinitrobenzoyl chloride, cyanoethylation with acrylonitrile in the presence of a base catalyst, and urethane formation with isocyanates.

Upon reaction of 2-(o-vinylphenoxy)ethanol with methacrylyl and acrylyl chlorides gave another set of non-conjugated dienes, 2-(o-vinylphenoxy)ethyl methacrylate and acrylate. Radical or photo-polymerization of the methacrylate and acrylate yielded polymers which were soluble in most of the polar organic solvents and had extremely high melting points. Spectroscopic evidence showed that these polymers contained only a very small degree of unsaturation. All the evidence suggested that these polymers consisted essentially of cyclic repeating units, which were presumably ten-membered rings.
CHAPTER I
INTRODUCTION

General Background

(2-Vinylxyethoxy)styrenes (I) were first synthesized along with their β-nitro analogs, (2-vinylxyethoxy)-β-nitrostyrenes (II), by Thompson in 1962: Nash had earlier attempted the synthesis of o- and p-(2-vinylxyethoxy)-β-nitrostyrenes. These styrene derivatives were prepared at that time for two purposes: (1) studies on their interesting molecular properties and (2) their suitability as ideal models for two-stage polymerization. Thompson finished, however, only the first goal and left the second part pending.

\[
\begin{align*}
\text{HC=CH}_2 & \quad \text{NO}_2 \\
\text{OCH}_2\text{CH}_2\text{OCH=CH}_2 & \quad \text{OCH}_2\text{CH}_2\text{OCH=CH}_2 \\
\text{o-, m-, and p-} & \quad \text{OCH}_2\text{CH}_2\text{OCH=CH}_2 \\
\text{(I)} & \quad \text{(II)} \\
\end{align*}
\]

It was not until 1971 that Schwietert studied the two-stage polymerization of the (2-vinylcyethoxy)-β-nitrostyrenes via independent anionic and cationic initiation. Studies on the polymerization of the (2-vinylxyethoxy)-styrenes, not yet undertaken, provided an interesting...
research subject, which was undertaken by the author when he entered the University of Florida in 1970.

The prior literature concerning the objective studies of the title compounds (I) and their related derivatives will be described in the following sections as: (a) two-stage polymerization, (b) chemical reactions of polymers, and (c) cyclopolymerization of unsymmetrical dienes. Although these subtitles appear to be different, they are actually related to each other as a whole for the title compounds under investigation.

Two-Stage Polymerization

The industrial importance of two-stage polymerizations has been demonstrated in the vulcanization of rubber, and in the thermosetting of phenol-formaldehyde, urea-formaldehyde, and alkyd polymers. In the area of vinyl polymerization, Mark\(^4\) has first shown that when vinyl n-propyl ketone is copolymerized with 10% of vinyl allyl ketone, linear polymer chain-molecules are formed primarily through the more readily polymerized vinyl group only, leaving the less reactive allyl groups intact. Butler and his coworkers\(^5\)-\(^\text{7}\) demonstrated later that allyl ethers of allyl substituted phenols and vinyl ethers of unsaturated alcohols could be polymerized selectively via cationic initiation to give thermoplastic polymers containing residual unsaturated groups. The resulting linear polymers, which possessed the allyl-type double bond, were then crosslinked or thermoset by radical initiation. A typical reaction sequence is shown in Equation (1).
After the reactivity of many of the important olefinic monomers toward radical or ionic initiation became clear, more investigations on a variety of non-conjugated diolefins appeared. Among these works, β-vinylxyethyl methacrylate was reported to react differently to cationic and anionic initiations, yielding soluble polymers of different structures. Similarly, it has been shown that allyl methacrylate and acrylate were polymerized with typical anionic initiators and with lithium dispersion in tetrahydrofuran to provide soluble polymers having essentially the same structure, comprising a polymethacrylate or polyacrylate backbone with pendent allyl groups. In addition, a few para-substituted styrenes have been polymerized anionically or cationically to linear polymers. Subsequent polymerization across the pendent vinyl or acetylenic groups always led to crosslinking the system.

More recently, Schwietert polymerized (2-vinyl-oxethoxy)-β-nitrostyrenes selectively through the nitrovinyllic moiety or the vinyl ether moiety via anionic or cationic initiation, respectively. The resulting linear polymers obtained from cationic initiation were subsequently
crosslinked through the pendent β-nitrovinyl groups by anionic polymerization. The reaction sequence is shown in Equation (2). The o-isomer could not be anionically polymerized under the same conditions as those of the m- and p-isomers. Evidence was presented to support the conclusion that the pendent vinyloxyethoxy group exerted an "ortho effect," which was believed to be a steric effect, on its adjacent β-nitrovinyl group, thus preventing the polymerization.

**Chemical Reactions of Polymers**

Long since the nitration of cellulose was conducted in 1854, the chemical reactions or chemical modifications of polymers have been an important branch of synthetic polymer chemistry. In general, most synthetic reactions of polymers are carried out for two purposes: (1) preparation of polymers with special functional groups or (2) modification of the polymer backbone chain in order to achieve special or
unusual effects not readily obtainable in polymerization reactions. The nitrated cellulose or cellulose nitrate, which is known for its much greater endurance and impact resistance in many respects than cellulose itself, served as a good example of the first objective. On the other hand, poly(vinyl alcohol) (III), which is a typical well-known example of a polymer whose monomer does not exist, exemplifies the second purpose.

\[
\text{Poly}(\text{vinyl alcohol}) \quad \text{with its free hydroxy groups offers considerable versatility for chemical transformation.}^{17} \quad \text{For example, it is capable of undergoing esterification to its parent poly(vinyl acetate) (IV) and many other polyesters, acetal formation to poly(vinyl butyral) (V), and cyanoethylation with acrylonitrile to poly(vinyl \textit{\beta}-cyanoethyl ether) (VI).}
\]
Cyclopolymerization of Unsymmetrical Dienes

The polymerization of non-conjugated dienes generally resulted in the formation of either linear polymers containing unreacted double bonds or crosslinked polymers. Butler and his coworkers\textsuperscript{18,19} first found that several diallyl quaternary ammonium salts polymerized to yield soluble and hence linear polymers containing little or no residual unsaturation, and involving an alternating intramolecular-intermolecular chain propagation. To describe this new polymerization reaction, the term "cyclopolymerization" has now been adopted. Since then, a great number of related papers have emerged and the new field has rapidly developed. A general reaction mechanism is shown in Equation (3). When

\[
\text{(VII)} \quad \text{R*} \quad \text{(VIII)} \quad \text{R} \quad \text{(IX)} \quad M \quad \{\text{cyclotetramer}\}^n
\]

a suitable initiator reacts with one double bond of a diene monomer (VII), a anion, cation, or free radical-containing intermediate (VIII) is formed. This intermediate then reacts intramolecularly with the remaining double bond to close the ring and produces a different reactive species (IX). The reaction propagates by attacking another monomer molecule and performing repeatedly, leading eventually to a linear, saturated polymer comprised of cyclic repeating units.
After Butler's initial investigations, it was soon demonstrated that a variety of symmetrical 1,5- or 1,6-dienes could be polymerized to soluble saturated polymers. Their structures were mainly composed of five- or six-membered rings with methylene groups alternating along the linear polymer chain. A few typical examples, such as the disubstituted 1,6- and 1,7-heptadienes (X),\textsuperscript{20-23} 1,2-divinylbenzene (XI),\textsuperscript{24} and acrylyl and methacrylyl anhydride (XII),\textsuperscript{25} are shown as follows.

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{R} \quad \text{H}_2\text{C} \quad \text{R} \\
& \quad (\text{CH}_2)_n \quad & \quad (\text{CH}_2)_n \\
\end{align*}
\]

\[
n = 2, \text{R} = \text{H}, \text{CO}_2\text{CH}_3, \text{or C}_6\text{H}_5
\]

\[
n = 3, \text{R} = \text{H}, \text{CO}_2\text{CH}_3, \text{or C}_6\text{H}_5
\]

\[
(X)
\]

\[
\begin{align*}
\text{R} & \quad \text{R} \\
\end{align*}
\]

\[
(XI)
\]

\[
\begin{align*}
\text{R} & \quad \text{R} \\
\end{align*}
\]

\[
(XII)
\]

\[
R = \text{H} \text{ or CH}_3
\]

(XII)
Symmetrical non-conjugated dienes, which were separated by more than three atoms, showed less tendency to form cyclopolymer. Holt and Simpson studied the polymerization of a series of diallyl esters (XIII) by radical initiation.

\[
\text{H}_2\text{C}=\text{CHCH}_2\text{O}_2\text{C}-(\text{CH}_2)_n-\text{CO}_2\text{CH}_2\text{CH}={\text{CH}}_2
\]

\[
\text{CO}_2\text{CH}_2\text{CH}={\text{CH}}_2
\]

\[
n = 0 - 8
\]

(XIII) (XIV)

They found that the intramolecular reaction did occur although the degree of cyclization was low. The three isomeric diallyl phthalates (XIV) were also studied. Diallyl terephthalate turned out to be crosslinked after the polymerization. Under the same reaction conditions, the o-isomer way cyclized to 41% and gave a soluble polymer. The explanation was that "a minimum of ten atoms was required for ring-closure between substituents on para positions."

Schulz and Stanner studied the polymerization of three isomeric bis-\(\text{N-vinyl}\) compounds (XV). Similar to the previous case (XIV), the p-isomer was crosslinked while the o-isomer was polymerized to a soluble product with 70% cyclization. Recently one more example was demonstrated by

\[
\text{OCNHCH}={\text{CH}}_2
\]

\[
\text{OCCH}={\text{CH}}_2
\]

\[
\text{o-}, \text{ m-}, \text{ and p-}
\]

(XV) (XVI)
Azuma and Ogata. They studied the polymerization mechanism of three isomeric diacrylates (XVI) by radical and photo-initiation, finding that only the o-isomer yielded a soluble polymer.

In the literature, it was found that polymerization studies of unsymmetrical non-conjugated dienes were limited to six-membered and smaller ring formation. Butler et al. studied the free radical polymerization of unsaturated esters of maleic and furmaric acids (XVII), and found that the polymerization of such unsymmetrical non-conjugated dienes having double bonds of different reactivity resulted in some cyclization. By stopping the polymerization just before the gel point, a series of soluble polymers containing a considerable amount of cyclization (23-63%) were obtained. Schulz et al. prepared a 1:1 copolymer (XX) of allyl alcohol and acrylic acid by hydrolysis of the cyclo-polymer (XIX) obtained from allyl acrylate (XVIII). Since alternating copolymers could not be synthesized from direct copolymerization of the monomer pairs, cyclopolymerization of the unsymmetrical dienes would give rise to a new route to the synthesis of alternating copolymers, which would be otherwise unobtainable.
Trossarelli et al. studied the radical polymerization of a series of unsymmetrical dienes mechanistically including allyl acrylate, allyl methacrylate, N-allylacrylamide, N-allylmethacrylamide, and vinyl crotonate. They found that these unsymmetrical dienes could be polymerized to soluble polymers containing appreciable amounts of cyclic units under suitable reaction conditions. In addition, they derived a general kinetic scheme for chain propagation of radical polymerization of unsymmetrical dienes, A-B, as follows.

(i) Intramolecular chain propagation reactions (cyclization)

\[ \text{A} \cdot \text{B} \xrightarrow{k_1} \text{A-B} \cdot \]
\[ \text{B} \cdot \text{A} \xrightarrow{k_2} \text{B-A} \cdot \]

(ii) Intermolecular chain propagation reactions

\[ \text{B-A} \cdot + \text{A} \text{B} \xrightarrow{k_3} \text{B-A-A} \cdot \text{B} \]
\[ \text{B-A} \cdot + \text{B} \text{A} \xrightarrow{k_4} \text{B-A-B} \cdot \text{A} \]
\[ \text{A-B} \cdot + \text{A} \text{B} \xrightarrow{k_5} \text{A-B-A} \cdot \text{B} \]
\[ \text{A-B} \cdot + \text{B} \text{A} \xrightarrow{k_6} \text{A-B-B} \cdot \text{A} \]
The arrangements of the structural units along the chains should be determined essentially by the relative rates of the above kinetic scheme assuming that the reaction characteristics of the growing polymer radicals depend primarily on the unit at the growing end and not on the length and composition of the chains. Under some basic assumptions, two meaningful equations, (4) and (5), were derived, where

\[ \frac{f_A}{f_B} = \frac{\alpha(M + \beta)}{(M + \gamma)} \]  

(4)

\[ \frac{f_L}{f_C} = \frac{(f_A + f_B)}{(f_{Ac} + f_{Bc})} = \frac{(aM^2 + bM)}{(M + c)} \]  

(5)

\( f_A, f_B, f_{Ac}, \) and \( f_{Bc} \) are the respective mole fractions in the increment of a polymer being formed at a given stage in the polymerization of the two linear structural units, \( -\cdot \cdot - \) and \( -\cdot \cdot - \), and the two cyclic structural units, \( -\cdot \cdot - \) and \( -\cdot \cdot - \); \( M \) is the monomer concentration; \( \alpha, \beta, \gamma \) and \( a, b, c \) are constants composed of rate constants; \( f_L/f_C \) is the ratio.
between the mole fractions of the linear and the cyclic units formed from the diene, A-B.

Equation (5) clearly predicts that the ratio $f_L/f_C$ will decrease with decreasing monomer concentration. In other words, $f_C$ will increase at the expense of $f_L$, i.e., polymerization tends to intramolecularly cyclize first, and then followed by intermolecular propagation.

It seems clear that for unsymmetrical dienes, the highest degree of cyclopolymerization could be achieved, first, from monomers having double bonds of comparable reactivity toward copolymerization but with little tendency to homopolymerize, and secondly, by diluting the monomer concentration and stopping the polymerization at low conversion to prevent it from going beyond the gel point.

**Research Objectives**

The purpose of this research work was first to study whether the (2-vinyloxyethoxy)styrenes (I) could be successfully polymerized by means of two-stage polymerization. It would be important to understand the reactivity of the two different double bonds, the styryl and the vinyl ether, involved in the molecules under study. It is known that styrene and methoxystyrenes are susceptible to anionic, cationic, and free radical initiations and vinyl ethers are only susceptible to cationic initiation. With all the previously described precedents examined, it was foreseeable that the (2-vinyloxyethoxy)styrenes would be capable of
being polymerized through only the styryl double bond by appropriate anionic initiators while leaving the vinyl ether moiety unreacted. The expected linear polymers thus formed could be crosslinked via the pendent vinyl ether groups by cationic initiation. In contrast with their β-nitro analogs, the (2-vinyl oxyethoxy) styrenes would form crosslinked polymers by starting with cationic initiation, because the styryl double bond is as susceptible to cationic initiation as is the vinyl ether group while the β-nitrovinyl group is not.

Provided that the (2-vinyl oxyethoxy) styrenes could be polymerized through only the styryl double bond, the pendent vinyl ether groups on the polymer side-chains would remain intact and the polymer would be linear and thus soluble. Since vinyl ethers are known to undergo many chemical reactions, the vinyl ether groups on the polymer side-chains are expected to behave similarly. One of the most interesting reactions seemed to be the hydrolysis of the vinyl ether in the presence of a catalytic amount of acid to its corresponding alcohol and acetaldehyde. A general equation is shown in Equation (6). By this means,

\[
R-0-CH=CH_2 \xrightarrow{H_3O^+} R-O-H + CH_3CHO \tag{6}
\]

the vinyloxy-containing polymer could be converted to a hydroxy-containing polymer if a suitable solvent could be found. The new polymer thus generated having a potentially reactive hydroxy group would be an interesting new material to study; for instance, it should be capable of undergoing
a great number of reactions similar to those reported earlier with poly(vinyl alcohol).^17

In addition to being prepared from the hydrolysis of the poly-(2-vinyl oxyethoxy)styrenes, the polyhydroxyethoxy-styrenes or more correctly, polyvinylphenoxyethanols, might also be obtained from their monomers by direct polymerization. The monomeric vinylphenoxyethanols could be prepared from the acid-catalyzed hydrolysis of the (2-vinyl oxyethoxy)-styrenes. Contrary to vinyl alcohol, which virtually does not exist, the vinylphenoxyethanols are vinyl aromatic alcohols and should be stable enough to be isolated. Surprisingly, a literature survey revealed merely two related examples, p-vinylphenylethyl alcohol^38 and p-vinylphenyl-alkylcarbinols,^39 along with their respective polymers. Therefore, the synthesis of the monomers themselves would be an interesting work.

If the vinylphenoxyethanols are available, more interesting work might be undertaken along this line in view of the great versatility for chemical transformation offered by the reactive hydroxy group. By reacting with acrylyl chloride, the vinylphenoxyethanols could be converted to their corresponding acrylates. In contrast with the (2-vinyl oxyethoxy)styrenes in which the two unsaturated double bonds have extremely different reactivity ratios in radical copolymerization,^40 the two unsaturated double bonds in the vinylphenoxyethyl acrylates, i.e., the styryl and the acrylic, have fairly similar reactivity ratios.^41
As previously mentioned, when the two unsaturated double bonds of an unsymmetrical diolefin have comparable reactivity toward copolymerization, they tend to cyclopolymerize. Besides, the literature has not revealed any example of large-ring cyclopolymers made from unsymmetrical dienes that are separated by more than three atoms. Hence, the attempt to synthesize and cyclopolymerize the vinylphenoxyethyl acrylates, particularly, 2-(o-vinylphenoxy)ethyl acrylate, which would be structurally favorable, seemed to be very challenging.
CHAPTER II
RESULTS AND DISCUSSION

Synthesis and Polymerization of o-, m-, and p-(2-Vinylxoyethoxy)styrenes

Synthesis of o-, m-, and p-(2-Vinylxoyethoxy)styrenes

The (2-vinylxoyethoxy)styrenes (I) were prepared essentially according to the methods given by Thompson with only minor modification. A general reaction scheme is shown in Equation (7). The hydroxybenzaldehydes (XXI) were

\[
\begin{align*}
&\text{CHO} \quad \text{CHO} \quad \text{CHO} \\
&\text{OH} \quad \text{OH} \quad \text{OH} \\
&\text{o-}, \text{m-}, \text{and p-} \\
&\text{(XXI)} \quad \text{(XXII)} \quad \text{(XXIII)}
\end{align*}
\]

first converted to their respective potassium salts (XXII) by treating with an equivalent amount of alcoholic potassium hydroxide. The potassium salts were hygroscopic and had to be dried thoroughly in a vacuum oven before use. The second
step of the reaction was carried out nicely in N,N-dimethylformamide (DMF) under mild reaction conditions. The (2-vinyloxyethoxy)benzaldehydes (XXIII) were obtained in good yields (70-80%). The Wittig reaction\textsuperscript{42,43} was employed to accomplish the last step conversion. Ortho- and m-(2-vinyl oxyethoxy)styrene were liquids at ambient temperature and their boiling points were only slightly lower than those of their corresponding benzaldehyde precursors at reduced pressure. Therefore, their purification by fractional distillation was best achieved by using a high efficiency spinning band column to assure the highest possible purity and yields. Like styrene, these styrene derivatives were also thermally unstable compounds. During the distillation period, the crude products became viscous and obviously had polymerized to some extent even though an inhibitor was used. Cuprous chloride was the most effective inhibitor among those tested; its extremely high boiling point (1366°C) caused no contamination of the products. The yields of this step were low (30-40%). The physical properties of the (2-vinyl oxyethoxy)styrenes agreed very well with those obtained by Thompson.\textsuperscript{1} The NMR spectra of o-, m-, and p-(2-vinyl oxyethoxy)styrenes are shown in Figures 1, 2, and 3, respectively.

**Anionic Polymerization of o-, m-, and p-(2-Vinyl oxyethoxy)styrenes**

All three isomeric monomers were polymerized successfully through use of sodium naphthalene radical anion\textsuperscript{44-47} in tetrahydrofuran (THF) at low temperatures. A general re-
Figure 1. NMR Spectrum of o-(2-Vinyl oxyethoxy)styrene
Figure 2. NMR Spectrum of m-(2-Vinyloxyethoxy)styrene
action sequence is shown in Equation (8). In the case of

the p-isomer, -50°C seemed to be the lowest optimum temperature. At temperatures lower than -50°C the p-isomer precipitated out of the solvent even though the solution concentration was fairly low (approx. 10%). After polymerization, the polymeric o- and p-isomers were isolated and purified as white powdery solids. The m-isomer, however, formed a soft gum, although its molecular weight was comparable to those of the o- and p-isomers. The soft appearance of the polymeric m-isomer was probably due to its glass-transition temperature which is lower than ambient temperature. The poly-(2-vinyl oxyethoxy)styrenes (XXIV) were high molecular weight linear polymers as indicated by their molecular weight and great solubility in most common organic solvents. With respect to the solubility characteristics of these polymers, they were found to be soluble in benzene, carbon tetrachloride, chloroform, 1,4-dioxane, N,N-dimethylformamide, tetrahydrofuran, etc., but they were insoluble in diethyl ether, methanol, and petroleum ether. It should be noted that the o- and m-isomers yielded stable polymers which did not change
their solubility in air over a long period of time. The polymeric p-isomer was, however, very unstable in air and became partially insoluble within a short period of time (a few days), presumably caused by air oxidation through the unsaturated vinyl ether moiety on the polymer side-chains thus leading to crosslinking. The partially soluble polymeric p-isomer was extracted with benzene and the insoluble particles were filtered off to give a clear solution. Reprecipitation from low-boiling petroleum ether yielded up to 40% of the original weight of the polymer. It was very surprising that this 40% soluble part could stay in air without changing its solubility as long as the polymeric o- and m-isomers, yet the cause was not clear. Since the insoluble part of the p-isomer had nearly the same infrared absorptions and softening point as the soluble portion, it appeared that the insoluble part of the polymer was only slightly crosslinked. The physical properties of these anionically initiated polymers are shown in Table 1.

The conclusion that anionic polymerization occurred only through the styryl double bonds of the (2-vinylxethoxy)styrenes was also supported by spectroscopic evidence. The NMR spectrum of poly[p-(2-vinylxethoxy)styrene] is shown in Figure 4 (page 21), as an example, in comparison with that of its parent monomer (see Figure 3, page 20). The infrared spectra of the polymers lacked the absorptions at 1420 and 910 cm⁻¹, characteristic of the C-H bend of the styryl double bond, but the absorptions at 1640, 1620, 1200,
Table 1
Anionic-Initiated Polymerization
of o-, m-, and p-(2-Vinlyoxyethoxy)styrenes

| Monomer | Run No. | Conc. (THF) w/v, % | Initiator Concentration \(a\) & Conc., mmole | Temp., Conv. \(\%\) & Conv., T \(\circ\) & \([\eta]\), d1/g. & \(\bar{M}_n, b\) \(x 10^{-4}\) & \(\bar{M}_n, c\) \(x 10^{-4}\) & MWD, \(d\) & \(\bar{M}_w/\bar{M}_n\) |
|---------|---------|-------------------|----------------------------------|------------------|------------------|------------------|------------------|------------------|------------------|-----------------|
| Ortho   | I       | 25                | 0.37                             | -78              | 94               | 80-85            | 0.438            | 24.5             | 4.3              | 1.16            |
| Meta    | II      | 10                | 0.92                             | -78              | 83               | 35-40            | 0.395            | 10.8             | 1.4              | 1.74            |
| Meta    | III     | 25                | 0.76                             | -45              | 100              | 35-40            | 0.619            | 16.3             | 3.9              | 1.97            |
| Para    | IV      | 6                 | 0.34                             | -45              | 84               | 45-50            | -                | -                | 1.8              | -               |
| Para    | V       | 10                | 0.39                             | -45              | 93               | 45-50            | 0.155            | 9.19             | 1.4              | 1.11            |

\(a\) Sodium naphthalene; \(b\) By membrane osmometry; \(c\) Calcd. by Equation (9); \(d\) By gel permeation chromatography
and 815 cm\(^{-1}\), characteristic of the vinyl ether double bond, were still present. Whether the absorption at 1625 cm\(^{-1}\), characteristic of the C=C stretch of the styryl double bond, and the absorption at 990 cm\(^{-1}\), characteristic of the C-H out of the plane bend of the styryl double bond were still present, could not be verified due to the interference by the adjacent strong vinyl ether absorption bands. The ultraviolet spectra of the polymers were different from those of their corresponding monomers. The K bands, caused by the styrene moiety of the monomers in the region of 250-260 nm disappeared in the polymers. The B bands, typical of benzene nuclei containing auxochromophores, were shifted from 290-300 nm in the monomers to 275-285 nm in the polymers. The blue shifts clearly indicated that the polymeric molecules were less conjugated than their respective monomeric molecules. The absorption maxima (\(\lambda_{\text{max}}\)), molar absorbance (A.), and molar absorptivity (\(\epsilon\)) of the monomers and of the polymers are listed in Table 2. The ultraviolet spectra of the polymers are compared with those of their respective polymers as shown in Figures 3, 4, and 5.

**Characterization of the Poly-(2-vinylxethoxy)styrenes**

The poly-(2-vinylxethoxy)styrenes obtained by anionic initiation were well characterized. In addition to the routine intrinsic viscosity measurements, each polymer was characterized by molecular weight determination and gel permeation chromatography. The data are shown in Table 1,
### Table 2
Tabulation of Maxima in Ultraviolet Spectra

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conc. (^a) M. ( \times 10^5 )</th>
<th>( \lambda_{\text{max}} ) nm</th>
<th>A.</th>
<th>( \varepsilon_{\text{max}} )^b x ( \times 10^{-4} )</th>
<th>( \log \varepsilon_{\text{max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-(2-Vinylcarbonylethoxy)styrene</td>
<td>5.87</td>
<td>248</td>
<td>0.667</td>
<td>1.14</td>
<td>4.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>0.236</td>
<td>0.402</td>
<td>3.64</td>
</tr>
<tr>
<td>m-(2-Vinylcarbonylethoxy)styrene</td>
<td>8.32</td>
<td>249</td>
<td>0.89</td>
<td>1.07</td>
<td>4.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>295</td>
<td>0.72</td>
<td>0.240</td>
<td>3.38</td>
</tr>
<tr>
<td>p-(2-Vinylcarbonylethoxy)styrene</td>
<td>2.00</td>
<td>261</td>
<td>0.73</td>
<td>2.55</td>
<td>4.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>290</td>
<td>0.23</td>
<td>0.280</td>
<td>3.54</td>
</tr>
<tr>
<td></td>
<td>10.00</td>
<td>290</td>
<td>0.28</td>
<td>0.280</td>
<td>3.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>301</td>
<td>0.17</td>
<td>0.170</td>
<td>3.23</td>
</tr>
<tr>
<td>Poly[o-(2-vinylcarbonylethoxy)styrene]</td>
<td>20.3</td>
<td>273.5</td>
<td>0.76</td>
<td>0.207</td>
<td>3.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>279.5</td>
<td>0.37</td>
<td>0.183</td>
<td>3.26</td>
</tr>
<tr>
<td>Poly[m-(2-vinylcarbonylethoxy)styrene]</td>
<td>45.6</td>
<td>273.5</td>
<td>0.385</td>
<td>0.194</td>
<td>3.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>279.5</td>
<td>0.81</td>
<td>0.178</td>
<td>3.25</td>
</tr>
<tr>
<td>Poly[p-(2-vinylcarbonylethoxy)styrene]</td>
<td>40.8</td>
<td>277.5</td>
<td>0.66</td>
<td>0.161</td>
<td>3.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>285</td>
<td>0.55</td>
<td>0.135</td>
<td>3.13</td>
</tr>
</tbody>
</table>

---

\( a \). Molar concentration of the solute in 1,4-dioxane

\( b \). Calculated by the Beer-Lambert Law, \( A = \varepsilon c b \)
Figure 5. Ultraviolet Spectra of o-(2-Vinyloloxethoxy)styrone and the Anionically Initiated Polymer of that Compound
Figure 6. Ultraviolet Spectra of m-(2-Vinylxyethoxy)styrene and the Anionically Initiated Polymer of that Compound
Figure 7. Ultraviolet Spectra of \( p-(2\text{-Vinlyoxyethoxy})\text{styrene} \) and the Anionically Initiated Polymer of that Compound.
Molecular weight determination was measured by membrane osmometry, hence the molecular weight obtained was the number-average molecular weight, $\bar{M}_n$. These polymers had fairly high molecular weights ranging from $9 \times 10^4$ for the p-isomer to $2.5 \times 10^5$ for the o-isomer.

The number-average molecular weight of a polymer is theoretically calculable if the polymerization is obtained by anionic initiation without chain termination, i.e., "living" anionic polymerization. Equation (9) is suitable for anionic polymerization via a bifunctional chain propagation mechanism; for example, the polymerization of styrene by sodium naphthalene in tetrahydrofuran at low temperature. Equation (9) should be applicable to the present system assuming the polymerization of the (2-vinylxyethoxy) styrenes did follow the bifunctional propagation mechanism. Since the mechanism of the anionic polymerization with sodium naphthalene is well known and all the phenomena characteristic of the "living" polystyryl propagating anion and the near 100% conversion were observed, the assumption seemed to be very reasonable. According to Equation (9), the calculated $\bar{M}_n$'s were $4.3 \times 10^4$ for the o-isomer, and $1.4 \times 10^4$ for the p-isomer. Compared with the true $\bar{M}_n$ determined by membrane osmometry, the calculated values were only about 20% as much.
as the true values. This would appear to indicate that merely 20% of the added initiator was actually involved in the polymerization; the remaining 80% could have been either destroyed or not reacted at all. Morton and Milkovich\(^\text{45}\) have studied homogeneous anionic polymerization of styrene in tetrahydrofuran using sodium naphthalene as an initiator, and found an average initiator loss about 50% after mixing the initiator, solvent, and monomer. Among the initiator losses, they estimated that approximately two-thirds was lost even before adding the monomer; the following addition of the monomer accounted for the remaining one-third loss. In their studies Morton and his coworker, using very subtle vacuum line techniques, could not prevent 50% initiator loss through termination by impurities. By comparison, the 80% loss obtained here, which was presumably caused by less subtle vacuum line techniques, should be reasonable and acceptable, at least from the standpoint of the synthetic approach.

Molecular weight distribution of the polymers was determined by gel permeation chromatography (GPC).\(^\text{49-50}\) The results showed that the o- and p-isomers gave fairly narrow distribution curves and accordingly had a value of \(\bar{M}_w/\bar{M}_n\) close to unity. The m-isomer, however, gave a somewhat broader distribution curve and showed no improvements after further attempts to synthesize it. The difference in molecular weight distribution between these isomeric polymers
is presently not clear, but it was suspected that the difference was probably caused by their difference in reactivity and the not very subtle techniques used. The molecular weight distribution curves of the three isomeric poly-(2-vinylxyethoxy)styrenes are shown in Figures 8, 9, and 10, respectively.

Radical Polymerization of o-, m-, and p-(2-Vinylxyethoxy)-styrenes

It was a little surprising that the (2-vinylxyethoxy)-styrenes also yielded linear polymers via free radical initiation. Although vinyl ethers could not be homopolymerized by radical initiators,\textsuperscript{8} they have been reported to copolymerize with many other vinyl monomers,\textsuperscript{40,50-54} such as acrylonitrile, methyl acrylate, styrene, vinyl acetate, vinyl chloride, etc. The reactivity ratios of vinyl ethyl ether (M\textsubscript{1}) and styrene (M\textsubscript{2}) were r\textsubscript{1}~\textasciitilde{}0 and r\textsubscript{2}~\textasciitilde{}>50, respectively.\textsuperscript{40} The extremely different reactivity ratios of the vinyl ether and styrene indicate that once a vinyl ether monomer radical (M\textsubscript{1}•) is formed, it tends to react with a styrene molecule rather than to react with another molecule of its own; on the contrary, a styrene monomer radical (M\textsubscript{2}•) tends to react with another styrene molecule.\textsuperscript{55} As a result, one may predict that the polymer formed at low conversion must essentially consist of styrene units. However, the vinyl ether could be incorporated into the polymer chain to some extent if the polymerization were allowed to proceed to high conversion. The only reasonable explanation seemed to be
Figure 8. Molecular Weight Distribution Curve of Poly[o-(2-vinloxyethoxy)styrene]
Figure 9. Molecular Weight Distribution Curve of Poly[m-(2-vinyl oxyethoxy)styrene]
Figure 10. Molecular Weight Distribution Curve of Poly[p-(2-vinylloxyethoxy)styrene]
that the vinyl ether moiety in the (2-vinylxyethoxy)styrenes was initiated too slowly to compete with the styrene moiety and thus acted negligibly upon crosslinking the system even at the fairly high conversion.

The spectroscopic evidence and solubility characteristics proved that the vinyl ether moiety was intact. The infrared spectra of the radically initiated polymers were identical to those of the anionically initiated polymers. The continued presence of the strong absorptions at 1640, 1620, and 1200 cm\(^{-1}\) due to the vinyl ether double bonds eliminated any possibility that cyclopolymerization had occurred. As expected, these radical-initiated polymers had the same solubility characteristics as the anionic-initiated polymers did. Their physical properties are shown in Table 3.

As previously mentioned\(^2\), o-(2-vinylxyethoxy)-\(\beta\)-nitrostyrene could not be anionically polymerized by sodium ethoxide due to the ortho-vinylxyethoxy substituent which presumably exerted an "ortho effect" on its nearby \(\beta\)-nitrovinyl moiety. It should be noted that, contrary to its \(\beta\)-nitro analog, o-(2-vinylxyethoxy)styrene could be polymerized either anionically or radically as well as its m- and p-isomers. Apparently the so-called ortho effect was not present here in this molecule as far as the reaction conversion was concerned. It is believed that it was the \(\beta\)-nitro group that made the drastic difference in polymerizability between the two structurely similar compounds.
<table>
<thead>
<tr>
<th>Monomer</th>
<th>[M]/[S], w/ v, %</th>
<th>[I]/[M], w/ w, %</th>
<th>Conversion, %</th>
<th>[n], d1/g. in C6H6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ortho</td>
<td>15</td>
<td>1</td>
<td>43</td>
<td>0.332</td>
</tr>
<tr>
<td>Meta</td>
<td>15</td>
<td>1</td>
<td>57</td>
<td>0.224</td>
</tr>
<tr>
<td>Para</td>
<td>15</td>
<td>1</td>
<td>39</td>
<td>0.222</td>
</tr>
</tbody>
</table>

*Azobisisobutyronitrile*
Post-Cationic Polymerization of the Poly-(2-vinylxoyethoxy)-styrenes

The three isomeric polymers were further polymerized by boron trifluoride in toluene at -78°C. In order to achieve possible ladder polymerization instead of crosslinking, the cationic initiation was conducted at very low concentration (approx. 1% w/v). The polymeric products were pale yellow amorphous solids and did not melt below 300°C. They were found to be insoluble in all solvents tested though they occasionally swelled. Both the very high melting temperature and the non-solubility characteristics indicated that these polymers had very rigid, three-dimensional molecular structure, i.e., they had been crosslinked.

The infrared spectra of the polymers showed the lack of all the absorption bands typical of the vinyl ether moiety. The lack of the vinyl ether absorption indicated that the polymerization had gone to completion. The physical properties of these crosslinked polymers are shown in Table 4.

Butler and Ferree\textsuperscript{56} have studied the mechanism of crosslinking poly[m-(2-vinylxoyethoxy)styrene] by photo-initiation. Preliminary results showed that irradiations of the polymer in the presence of acceptors, such as chloranil or tetrachlorophthalic anhydride (TCPA), in acetonitrile under dry oxygen-free conditions yielded rapid precipitation of crosslinked polymers, which showed the same spectroscopic and physical characteristics as the cationically crosslinked poly[m-(2-vinylxoyethoxy)styrene].
Table 4
Cationic-Initiated Crosslinking of Poly-(2-vinlyoxyethoxy)styrenes

<table>
<thead>
<tr>
<th>Polymeric Precursor</th>
<th>[M]/[S], w/v, %</th>
<th>Initiator (BF₃), ml.</th>
<th>Reaction Conditions</th>
<th>Conversion %</th>
<th>Discoloration of Solid, °C</th>
<th>Tₘ, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ortho</td>
<td>1</td>
<td>3.0</td>
<td>Toluene, -78⁰</td>
<td>94</td>
<td>295-300</td>
<td>&gt;300</td>
</tr>
<tr>
<td>Meta</td>
<td>1</td>
<td>2.5</td>
<td>Toluene, -78⁰</td>
<td>88</td>
<td>295-300</td>
<td>&gt;300</td>
</tr>
<tr>
<td>Para</td>
<td>1</td>
<td>0.8</td>
<td>Toluene, -78⁰</td>
<td>83</td>
<td>290-300</td>
<td>&gt;300</td>
</tr>
</tbody>
</table>
Synthesis and Polymerization of o-, m-, and p-Vinylphenoxyethanols

Polyvinylphenoxyethanols from Hydrolysis of Poly-(2-vinloxyethoxy)styrenes

As previously mentioned, Schwietert polymerized m- and p-(2-vinloxyethoxy)-β-nitrostyrenes with sodium ethoxide via anionic initiation producing the corresponding linear polymers. Although the pendent vinyl ether moiety on the polymer side-chains was intact as evidenced by the continued presence of its characteristic infrared absorption, those polymeric products were reported to be unstable in air and became insoluble in all solvents tried over a short period of time. D'Alelio and Hoffend\textsuperscript{13} have reported a similar finding with their polymeric styrene derivatives, which had unsaturated substituents at the para position.

The poly-(2-vinloxyethoxy)styrenes, which were prepared by either anionic or radical initiation as described before, were found to be quite stable in air as noted by their unchanging solubility over a long period of time (more than one-half year) except the p-isomer which gave only 40\% of the soluble polymer after standing in air for a few days. The contrast in stability of the poly-(2-vinloxyethoxy)-styrenes and those reported examples was remarkable, but the cause was not clear yet. In addition to the difference in stability of the poly-(2-vinloxyethoxy)styrenes and the poly-(2-vinloxyethoxy)-β-nitrostyrenes, their solubility characteristics were also different. While the former was
soluble in most common organic solvents, the latter was reported to be insoluble in most common organic solvents tried but was soluble in N,N-dimethylaniline and hexamethylphosphotriamide (HMPA).

Both the unusual stability and great solubility made the poly-(2-vinylxyethoxy)styrenes suitable for chemical reactions. They underwent acid-catalyzed hydrolysis nicely in a mixture of 10% dilute hydrochloric acid and 90% acetone, leading to the formation of polyvinylphenoxyethanols (XXV). The hydroxy-containing polymers were identified by spectroscopic evidence and elemental analyses. Their infrared spectra showed a strong broad absorption at 3400 cm\(^{-1}\), characteristic of the O-H stretch, and the lack of absorptions at 1640, 1620, and 1200 cm\(^{-1}\), characteristic of the vinyl ether moiety. The ultraviolet spectra of the polymers were, as expected, practically identical to those of their polymeric precursors, the poly-(2-vinylxyethoxy)styrenes. The infrared evidence and the elemental analysis indicated this polymer hydrolysis reaction to be complete. The NMR spectrum of poly[(o-vinylphenoxy)ethanol] is shown in Figure 11, page 46, to compare with that of its monomer (see Figure 12, page 47). A significant change, in many respects,
in the physical properties was noticed when the poly-(2-vinyl oxyethoxy)styr elenes were transformed into the polyvinyl phenoxyethanols. Besides the higher melting points and greater intrinsic viscosities than their respective polymeric precursors, the hydroxy-containing polymers showed only limited solubility characteristics. They were soluble in some polar solvents such as dimethylformamide and dimethyl sulfoxide, but were not as soluble in others like acetone, chloroform, methanol, and tetrahydrofuran, with the exception of the o-isomer which showed much greater solubility in these solvents than the m- and p-isomers. They all were found to be insoluble in less and non-polar solvents, such as benzene, carbon tetrachloride, and petroleum ether. Just like monomeric aromatic alcohols, these hydroxy-containing polymers were completely insoluble in water. Since dimethylformamide dissolved the polymers to give very clear solutions, solution casting from dimethylformamide solution could be used to make a clear, transparent polymer film. The physical properties of the polyvinylphenoxyethanols are shown in Table 5.

Synthesis of o-, m- and p-Vinylphenoxyethanols

Unlike poly(vinyl alcohol) whose monomer does not exist, the polyvinylphenoxyethanols could also be obtained from direct polymerization of their respective monomers, vinylphenoxyethanols (XXVI). These monomeric compounds could be prepared from hydrolysis of the (2-vinyl oxyethoxy) styrenes.
Table 5
Properties of Polyvinylphenoxyethanols from Polymer Hydrolysis

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Polymeric Precursor</th>
<th>Hydrolytic Conditions</th>
<th>Conversion %</th>
<th>T&lt;sub&gt;m&lt;/sub&gt;, °C</th>
<th>[n], dl/g. in DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-(o-Vinylphenoxy)-ethanol</td>
<td>o-(2-Vinyl oxy-ethoxy)styrene [n] = 0.438</td>
<td>90% Acidic Aq. acetone</td>
<td>97</td>
<td>170-180</td>
<td>0.485 (0.267 in THF)</td>
</tr>
<tr>
<td>2-(m-Vinylphenoxy)-ethanol</td>
<td>m-(2-Vinyl oxy-ethoxy)styrene [n] = 0.619</td>
<td>90% Acidic Aq. acetone</td>
<td>96</td>
<td>100-110</td>
<td>1.27</td>
</tr>
<tr>
<td>2-(p-Vinylphenoxy)-ethanol</td>
<td>p-(2-Vinyl oxy-ethoxy)styrene [n] = 0.155</td>
<td>90% Acidic Aq. acetone</td>
<td>93</td>
<td>155-165</td>
<td>0.219</td>
</tr>
</tbody>
</table>
Acid-catalyzed hydrolysis of the (2-vinylxyethoxy)styrenes went to completion within a short time as noted by the lack of the characteristic absorption bands of the vinyl ether group in the infrared and NMR spectra of the crude products.

The crude o- and m-isomers were extremely high-boiling liquids under ambient conditions. The first few attempts to purify them by using regular micro-distillation apparatus led to either failure or very low yields, because the crude products thermally polymerized very rapidly in the pot at the necessary high distillation temperature in vacuo, although an inhibitor was always used. Short path molecular distillation on a high vacuum line (approx. \(10^{-4}\) mmHg.) was later tried and found to be very effective as indicated by the much improved yields (~80%). The pure o-isomer crystallized in the cooling bath and did not melt at ambient temperature, but a further attempt to recrystallize it from low-boiling petroleum ether was unsuccessful. The p-isomer was isolated as a solid and could be recrystallized from low-boiling petroleum ether very well.

The molecular structures of the vinylphenoxyethanols were identified by spectroscopic evidence and elemental
analyses. The infrared spectra of these compounds showed in common a strong broad absorption at about 3400 cm\(^{-1}\), characteristic of the O-H stretch, but lacked the absorptions at 1640, 1620, and 1200 cm\(^{-1}\), characteristic of the vinyl ether moiety. Their NMR spectra showed a sharp singlet around $\delta$3.0, characteristic of the hydroxy proton. As expected, their ultraviolet spectra were nearly identical to those of their respective precursors. The NMR spectra of o-, m-, and p-vinylphenoxyethanols are shown in Figures 12, 13, and 14, respectively.

From the viewpoint of organic synthesis, the vinyl ether group played substantially the role of a protective functional group in the preparation of the vinylphenoxyethanols. If the vinyl aromatic alcohols are to be synthesized directly from their benzaldehyde analogs by the Wittig reaction, the strongly basic ylide would react with the reactive hydroxy protons. Therefore two moles of the Wittig reagent are required to react with one mole of the (2-hydroxyethoxy)benzaldehyde, which would be very inconvenient for large scale synthesis as well as lead to a waste of the ylide. Since the vinyl ether group is known to be inert to strong bases,$^{57}$ the vinyl ether groups in the (2-vinyloxyethoxy)benzaldehyde did not react with the ylide. The following acid-catalyzed hydrolysis demonstrated that the vinyl ether group could be easily and completely removed and thus caused no contamination of the products. It is note-
Figure 11. NMR Spectrum of Poly[2-(o-vinylphenoxy)ethanol]
Figure 13. NMR Spectrum of 2-(m-Vinylphenoxy)ethanol
Figure 14. NMR Spectrum of 2-(p-Vinylphenoxy)ethanol
worthy that this valuable utilization of the vinyl ether group as a protective group for the alcohol against strong base has not been cited in the known literature source.

Radical Polymerization of the o-, m-, and p-Vinylphenoxyethanols

The vinylphenoxyethanols were polymerized via free radical initiation to give their respective polymeric products. The infrared spectra of these radically initiated polymers were identical to those of the polymers obtained from the hydrolysis of the poly-(2-vinylphenoxyethoxy)styrenes; so were their solubility characteristics and melting points. This clearly indicated that the polyvinylphenoxyethanols could be either indirectly or directly prepared. A general reaction scheme is shown in Equation (10).

\[
\begin{align*}
HC &= CH_2 \\
\text{HC} &= \text{CH}_2 \\
\text{OCH}_2\text{CH}_2\text{OCH}=\text{CH}_2 &\rightarrow \text{OCH}_2\text{CH}_2\text{OH} \\
\text{(HC}-\text{CH}_2\text{)}_n &\rightarrow \text{OCH}_2\text{CH}_2\text{OH} \\
\text{HC} &= \text{CH}_2 \\
\text{OCH}_2\text{CH}_2\text{OCH}=\text{CH}_2 &\rightarrow \text{OCH}_2\text{CH}_2\text{OH}
\end{align*}
\]

(10)

properties of the radical-initiated polyvinylphenoxyethanols are shown in Table 6.

Chemical Reactions of the Polyvinylphenoxyethanols

The polyvinylphenoxyethanols could be converted to
Table 6

Conditions of Polymerization and Properties of the Radical-Initiated Polyvinylphenoxyethanols

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Polymerization Conditions</th>
<th>Conversion %</th>
<th>([n]), dl/g. in DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-(o-Vinylphenoxy)-ethanols</td>
<td>AIBN, 70°C, in Benzene</td>
<td>86</td>
<td>0.374 (0.196 in THF)</td>
</tr>
<tr>
<td>2-(m-Vinylphenoxy)-ethanols</td>
<td>AIBN, 60°C, in THF</td>
<td>58</td>
<td>1.85</td>
</tr>
<tr>
<td>2-(p-Vinylphenoxy)-ethanols</td>
<td>AIBN, 60°C, in THF</td>
<td>46</td>
<td>0.287</td>
</tr>
</tbody>
</table>
many of their polymeric derivatives by reacting their hydroxy functional groups with many known chemical reagents, such as acid halides, isocyanates, acrylonitrile in the presence of base catalyst, etc. A few typical reactions are described as follows.

Reaction with 3,5-dinitrobenzoyl chloride. Upon reacting with 3,5-dinitrobenzoyl chloride in the presence of pyridine, the hydroxy-containing polymers were converted to their respective dinitrobenzoyl esters as shown in Equation (11).

\[
\begin{align*}
\text{CH} & \text{CH}_2 \text{CH}_2 \text{OH} \\
\text{OCH}_2 \text{CH}_2 & \text{OH} \\
\text{OCH} & \text{CH}_2 \text{CH}_2 \text{OC} = O \\
\text{OCH} & \text{CH}_2 \text{CH}_2 \text{OC} = O \\
\end{align*}
\]

(XXVII)

The infrared spectra of these polyesters showed a strong carbonyl absorption at 1730 cm\(^{-1}\) and nitro group absorptions at 1540 and 1340 cm\(^{-1}\). No absorption in the region of the hydroxy group was observable. The elemental analyses showed that the found values were in good agreement with the calculated values of the poly(vinylphenoxyethyl 3,5-dinitrobenzoates) (XXVII). The solubility behavior of these polyesters was similar to that of their polymeric precursors. They were soluble in dimethylformamide, and were modestly soluble in other polar solvents, such as acetone, acetonitrile...
Table 7

Properties of Poly(vinylphenoxyethyl 3,5-dinitrobenzoates)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Polymeric Precursor</th>
<th>Reaction Conditions</th>
<th>Conversion %</th>
<th>Tₘ, °C</th>
<th>[n], d1/g. in DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ortho</td>
<td>2-(o-Vinylphenoxy)-ethanol</td>
<td>Ambient Temp., DMF</td>
<td>87</td>
<td>120-125</td>
<td>0.510</td>
</tr>
<tr>
<td>Meta</td>
<td>2-(m-Vinylphenoxy)-ethanol</td>
<td>Ambient Temp., DMF</td>
<td>91</td>
<td>80-95</td>
<td>0.665</td>
</tr>
<tr>
<td>Para</td>
<td>2-(p-Vinylphenoxy)-ethanol</td>
<td>Ambient Temp., DMF</td>
<td>89</td>
<td>90-100</td>
<td>0.379</td>
</tr>
</tbody>
</table>
trile, chloroform, dioxane, ethyl acetate, and tetrahydrofuran but were insoluble in benzene, carbon tetrachloride, ethyl ether, and petroleum ether. Their physical properties are shown in Table 7.

A few other polymer reactions were carried out with the o-isomer as an example as shown in Equation (12).

![Chemical structures](image)

**Reaction with acrylonitrile.** In the presence of a base catalyst, sodium methoxide, the hydroxy-containing polymer was converted to its cyanoethylated adduct by reacting with acrylonitrile under mild conditions ($40^\circ$C). Heating was necessary because no reaction was observed when the reaction was conducted at ambient temperature. The infrared spectrum of the polymer showed absorptions at 2250 and 1127 cm$^{-1}$ indicative of the presence of C=Н and aliphatic C-O-C, respectively. No absorption in the O-H region was observed. The physical properties of the polymer are shown in Table 8.
Reaction with isocyanates. Phenyl isocyanate upon reaction with the hydroxy-containing polymer yielded a polymer which showed infrared absorptions at 3330, 3290, and 1550 cm\(^{-1}\), characteristic of the N-H group, and absorption at 1650 cm\(^{-1}\), characteristic of the C=O group of the secondary amide. No broad absorption band in the O-H region was observed. The physical properties of the polymer are shown in Table 8.

After being treated with an equivalent amount of methylene bis(4-phenyl isocyanate), a solution of poly-[2-(o-vinylphenoxy)ethanol] became gelled the following day. The polymeric product thus obtained was found to be insoluble in all solvents tried. The infrared spectrum of the polymer showed all the absorption bands characteristic of the secondary amide, and absorption at 2250 cm\(^{-1}\), characteristic of the residual isocyanate groups. No O-H absorption was observed, an indication that the polymer was highly cross-linked.

Synthesis and Cyclopolymerization of 2-(o-Vinylphenoxy)ethyl Methacrylate and Acrylate

Synthesis of 2-(o-Vinylphenoxy)ethyl Methacrylate and Acrylate

The methacrylate and acrylate were prepared by esterification of 2-(o-vinylphenoxy)ethanol with acrylyl and methacrylyl chloride, respectively, as shown in Equation (13); however, they were purified differently.

\[
\begin{align*}
\text{R} & = \text{H or CH}_3 \\
\text{O} & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \ quad
Table 8
Properties of Polymeric Derivatives from Poly[2-(o-vinylphenoxy)ethanol]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Conversion %</th>
<th>(T_m, ^\circ C)</th>
<th>[(\eta)], dl/g. in DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>(XXVIII)</td>
<td>62</td>
<td>60 - 65</td>
<td>0.516</td>
</tr>
<tr>
<td>(XXIX)</td>
<td>94</td>
<td>170 - 180</td>
<td>0.574</td>
</tr>
<tr>
<td>(XXX)</td>
<td>--</td>
<td>&gt;300</td>
<td>--</td>
</tr>
</tbody>
</table>
During the preparation of the methacrylate, it was found that an impurity was always present in the crude products obtained from the different runs although methacrylyl chloride had been freshly distilled before use. This impurity could not be removed by evaporation under high vacuum, and attempts to separate it from the desired product by fractional distillation were unsuccessful, because the crude product had thermally polymerized in the pot before the impurity could be completely removed. The impurity seemed to be methacrylic anhydride as indicated by its infrared and NMR spectra. Purification by column chromatography was then tried and found to be successful as indicated by the TLC analysis. Subsequent molecular distillation on a high vacuum line yielded the pure product, but the yield was quite low. The infrared spectrum of the compound showed a strong absorption at 1720 cm\(^{-1}\), characteristic of the C=O stretch, and at 1170 cm\(^{-1}\), characteristic of the asymmetrical C-O stretch. No absorption in the O-H region was observable. The NMR spectrum of the compound, which showed the absence of the hydroxy proton, is shown in Figure 15.

In the case of the acrylate, the spectral analysis of the crude product did not show the presence of any impurities. It was simply purified by distillation on a high vacuum line to give the pure product, but the yield was not satisfactory. The molecular structure of this diene monomer was confirmed
by spectroscopic evidence and elemental analysis. The infrared spectrum of the compound showed a strong absorption at 1724 cm\(^{-1}\) due to the C=O stretch and 1185 cm\(^{-1}\) due to the asymmetrical C-O stretch. No infrared absorption corresponding to the O-H was observed. The NMR spectrum of the compound is shown in Figure 17.

**Cyclopolymerization of 2-(o-Vinylphenoxy)ethyl Methacrylate and Acrylate**

The methacrylate and acrylate were polymerized via free radical or photo-initiation in tetrahydrofuran at 60°C or ambient temperature, respectively. The polymeric products thus obtained were found to be soluble in chloroform, dimethylformamide, tetrahydrofuran, etc., and were still soluble after standing in air for a few months. The melting points of these polymers were extremely high (>300°C). Besides, the solid polymers showed somewhat crystalline appearance; however, preliminary investigation by X-ray diffraction did not reveal any crystallinity. The physical properties of the polymers are shown in Table 9.

The infrared spectra of the polymers, obtained from the methacrylate monomer, showed only a very small degree of unsaturation as evidenced by the presence of a very weak shoulder at 1630 cm\(^{-1}\) due to the C=C stretches of the styryl and acrylic double bonds, and by the absence of any absorption near 1410 cm\(^{-1}\) due to the =C-H bends of the styryl and acrylic double bonds. The absorptions at 1000 and 900 cm\(^{-1}\), characteristic of the =C-H out-of-plane bends of the
double bonds, were also hardly detectable. The infrared spectra of the radical and photo-initiated polymers, being compared with that of their monomer, are shown in Figure 19. The NMR spectrum of the radical-initiated polymer, as shown in Figure 16, showed the presence of two tiny peaks at δ6.1 and δ5.6 corresponding to the terminal protons of the methacrylic double bond, but the vinyl proton absorptions of the styryl double bond were hardly distinguishable from the noise. While the NMR absorptions in the region of the vinylic protons essentially disappeared, a broad absorption in the region of saturated aliphatic protons appeared.

The spectroscopic analyses of the polymers, obtained from the acrylate monomer, showed even less unsaturation than the methacrylate polymers did. This was evidenced by the barely observable absorptions due to the styryl and acrylic double bonds in the infrared spectra, and the hardly observable absorptions due to the vinylic protons in the NMR spectra, as shown in Figure 20 and Figure 18, respectively.

All the evidence presented, both physical and spectroscopic, have indicated that these polymers consisted essentially of the cyclic repeating units containing only a very small degree of unsaturation on the polymer side-chains. Although a quantitative determination of the degree of unsaturation was not undertaken due to the limited amount of the polymers available, it could be roughly estimated that the total degree of unsaturation should not be greater than 10% in accordance with the well-known instrumental
Table 9
Polymerization of 2-(o-Vinylphenoxy)ethyl Methacrylates and Acrylates

<table>
<thead>
<tr>
<th>Monomer</th>
<th>[M]/[S], w/v, %</th>
<th>[I]/[M], w/w, %</th>
<th>Temp., °C</th>
<th>Time, hrs.</th>
<th>Conversion, %</th>
<th>[n], d1/g. in THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methacrylate</td>
<td>5%, THF</td>
<td>AIBN, 0.5%</td>
<td>60</td>
<td>6</td>
<td>37</td>
<td>0.226</td>
</tr>
<tr>
<td>Methacrylate</td>
<td>5%, THF</td>
<td>hv</td>
<td>Ambient</td>
<td>4½</td>
<td>6.4</td>
<td>-</td>
</tr>
<tr>
<td>Acrylate</td>
<td>5%, THF</td>
<td>AIBN, 0.5%</td>
<td>60</td>
<td>3½</td>
<td>40</td>
<td>0.095</td>
</tr>
<tr>
<td>Acrylate</td>
<td>5%, THF</td>
<td>hv</td>
<td>Ambient</td>
<td>60</td>
<td>28</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 15. NMR Spectrum of 2-(o-vinylphenoxy)ethyl Methacrylate
Figure 17. NMR Spectrum of 2(o-Vinlyphenoxy)ethyl Acrylate
Figure 18. NMR Spectrum of Poly[2-(o-vinylphenoxy)ethyl acrylate]
Figure 19. Infrared Spectra of (A) 2-(o-Vinylphenoxy)ethyl Methacrylate (VPEM), (B) Radical-Initiated Polymer of VPEM, and (C) Photo-Initiated Polymer of VPEM
Figure 20. Infrared Spectra of (A) 2-((o-Vinylphenoxy)ethyl Acrylate (VPEA), (B) Radical-Initiated Polymer of VPEA, and (C) Photo-Initiated Polymer of VPEA
detectability inherent in the infrared and NMR spectrometry. A general reaction scheme is shown in Equation (14).

![Reaction Scheme](image)

\[ R = H \text{ or } CH_3 \]
CHAPTER III
EXPERIMENTAL

Equipment and Data

A Beckman DK-2A double-beam recording spectrophotometer was used to obtain ultraviolet spectra.

A Beckman IR-8 or a Beckman IR-10 infrared spectrophotometer was used to obtain infrared spectra.

A Varian A-60 NMR spectrometer was used to obtain NMR spectra using carbon tetrachloride ($\text{CCl}_4$) or deuterated chloroform ($\text{CDCl}_3$) as the solvent.

A Thomas-Hoover capillary melting point apparatus was used to determine the melting points of solid monomeric compounds, and the melting points reported are uncorrected.

A Fisher-Johns melting point apparatus was used to obtain the melting points of polymeric materials.

A Waters GPC 300 gel permeation chromatograph was used with calibrated polystyrene gel columns to obtain molecular weight distribution data.

A Mechrolab 502 high speed membrane osmometer was used to measure number-average molecular weight data.

A Cannon-Uhbelodhe semi-micro dilution viscometer (75/K620) was used to measure intrinsic viscosities, and the constant temperature bath was set at 30°C unless otherwise indicated.
A Hanovia 679-A-36 high pressure mercury vapor lamp (450 watts) was used as an irradiation source for photopolymerization.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee and by PCR, Incorporated, Gainesville, Florida.

Source and Methods of Purification of Reagents
Salicylaldehyde (practical) was obtained from Fisher and used without purification.

m-Hydroxybenzaldehyde (practical) was obtained from Pfaltz & Bauer and used without further purification.
p-Hydroxybenzaldehyde (practical) was obtained from Eastman Kodak and used directly.

2-Chloroethyl vinyl ether (practical) was obtained from Aldrich and purified by distillation under vacuum.

Methyltriphenylphosphonium bromide (reagent) was obtained from PCR and purified by drying over phosphorus pentoxide ($P_2O_5$) in a vacuum oven at 100°C before use.

n-Butyllithium (15% in n-hexane) was obtained from MCB and used directly.

Acrylyl and methacrylyl chlorides (reagent) were obtained from Aldrich and purified by distillation under nitrogen before use.

Monomer Synthesis

Synthesis of o-, m-, and p-(2-Vinloxyethoxy)styrenes

o-(2-Vinloxyethoxy)benzaldehyde. The potassium salt of
salicylaldehyde was prepared on a 1.0 mole scale. To a solution of 65.0 g. of 86.8 % potassium hydroxide in 500 ml. of absolute ethanol in a 1000 ml. round bottom flask was added a solution of 122 g. of salicylaldehyde in 100 ml. of absolute ethanol. A spontaneous exothermic reaction accompanied by the formation of precipitate was observed. The solvent was removed through rotary evaporation at reduced pressure, and any residual moisture was removed via the benzene-water azeotrope. The yellow crystalline solid was then dried in a vacuum oven at 80°C overnight. The yield was essentially quantitative.

To a 1000 ml. three-necked round bottom flask equipped with a thermometer, a mechanical stirrer, and a condenser protected by a drying tube were added 160 g. of the potassium salt, 116 g. (1.0 mole plus 10% excess) of 2-chloroethyl vinyl ether, and 400 ml. of anhydrous N,N-dimethylformamide. The reaction mixture was heated to 100°C and stirred at this temperature for 6 hours. At the end of the reaction, the mixture was cooled and then poured into 1500 ml. of water. The aqueous mixture was extracted with 300 ml. portions of diethyl ether three times, and the combined ethereal extracts were dried over anhydrous magnesium sulfate.

The ether was evaporated through a rotary evaporator, and the residual oily liquid was distilled under vacuum yielding 151 g. (78%) of a colorless liquid: b.p.: 114°C/0.17 mmHg. The infrared spectrum and physical properties of
this compound agreed with those obtained by Thompson.¹

The NMR spectrum (CCl₄) of the compound showed absorptions at 610.4 (singlet, 1H, CHO), 7.8-6.8 (multiplet, 4H, aromatic H), 6.45 (quartet, 1H, OCH=), and 4.35-3.94 (multiplet, 6H, =CH₂ & OCH₂CH₂O).

o-(2-Vinlyoxyethoxy)styrene. The methyl ylide was generated in situ as follows. In a 3000 ml. three-necked round bottom flask equipped with an addition funnel, a mechanical stirrer, a condenser protected by a drying tube, a gas inlet, and a rubber septum were placed 122 g. (0.33 mole) of dry methyltriphenylphosphonium bromide and 1200 ml. anhydrous ether. A gentle flow of dry nitrogen through the apparatus was maintained throughout the reaction. To the stirred ether suspension was added 235 ml. of n-butyllithium (15% in n-haxane) by using a 30 ml. syringe. The nearly clear orange ylide solution was formed at the end of the addition, and it was continuously stirred for 2 hours.

To the ylide solution was slowly added a solution of 64.5 g. (0.33) mole of o-(2-vinlyoxyethoxy)benzaldehyde in 200 ml. of anhydrous ether. The pale yellow slurry thus formed was stirred overnight. At the end of the reaction, 1000 ml. of water was added to the reaction mixture, and the aqueous layer was extracted with 250 ml. portions of ethyl ether three times. The combined ethereal solution was dried over anhydrous magnesium sulfate. After removal of the solvent on a rotary evaporator, the oily residue, in which a
small amount of cuprous chloride was added as an inhibitor, was fractionally distilled under vacuum through a 60 cm. spinning band column to yield 24.9 g. (40%) of a colorless liquid; b.p.: 90-92°C/0.70mmHg. The infrared and ultraviolet spectra of this compound as well as its physical properties agreed with those obtained by Thompson.1

The NMR spectrum (CCl₄) of the compound showed absorptions at δ7.43-6.55 (multiplet, 5H, aromatic H & PhCH=), 6.38 (quartet, 1H, OCH=, Jαβ cis = 7 Hz, Jαβ trans = 14.5 Hz), 5.64 & 5.16 (AB quartet, 2H, =CH₂, JAB = 1.7 Hz, JAX = 17.8 Hz, JBX = 11.0 Hz), and 4.25-3.72 (multiplet, 6H, OCH=CH₂ & OCH₂CH₂O).

m-(2-Vinyloxyethoxy)benzaldehyde. This compound was prepared from the potassium salt of m-hydroxybenzaldehyde and 2-chloroethyl vinyl ether by the procedure given above for o-(2-vinyloxyethoxy)benzaldehyde on a 0.6 mole scale. Vacuum distillation of the crude product gave 81.9 g. (71%) of the product; b.p.: 88-90°C/0.07mmHg. The liquid crystallized on standing and could be recrystallized from n-pentane to give a white crystalline solid; m.p.: 41.5-42°C.

The NMR spectrum (CCl₄) of the compound gave absorptions at δ9.90 (singlet, 1H), 7.40-6.98 (multiplet, 4H), 6.43 (quartet, 1H), and 4.35-3.87 (multiplet, 6H).

m-(2-Vinyloxyethoxy)styrene. This styrene derivative was synthesized on a 0.25 mole scale by the method used for o-(2-vinyloxyethoxy)styrene. Fractional distillation under vacuum through a spinning band column gave 17.7 g. (38%) of
a colorless liquid; b.p.: 73-74°C/0.10mmHg.

The NMR spectrum (CCl₄) of the compound gave absorptions at δ7.26-6.56 (multiplet, 5H, aromatic H & PhCH=), 6.43 (quartet, 1H, OCH=, Jₐ₋₇cis = 7.2 Hz, Jₐ₋₇trans = 13.8 Hz), 5.63 & 5.15 (AB quartet, 2H, =CH₂, Jₐ₋₇ = 1.3 Hz, Jₐ₋ₓ = 17.4 Hz, Jₓ₋ₓ = 10.5 Hz) and 4.28-3.71 (multiplet, 6H, OCH₂CH₂OH).

P-(2-Vinlyoxyethoxy)benzaldehyde. This benzaldehyde was prepared on a 0.5 mole scale by the method used for o-(2-vinlyoxyethoxy)benzaldehyde. Vacuum distillation of the crude product yielded 70.3 g. (73%) of the product; b.p.: 106°C/0.15mmHg. The liquid solidified on standing; m.p.: 40-41°C.

The NMR spectrum (CCl₄) of the compound gave absorptions at δ9.75 (singlet, 1H), 7.77-6.82 (multiplet, 4H), 6.43 (quartet, 1H), and 4.31-3.86 (multiplet, 6H).

p-(2-Vinlyoxyethoxy)styrene. This compound was prepared on a 0.25 mole scale by the method used for o-(2-vinlyoxyethoxy)styrene, but was purified differently. After the work-up, the crude solid residue was extracted with petroleum ether (b.p.: 30-75°C). Evaporation of the combined extracts to dryness gave a white crystalline solid, m.p.: 50-55°C. The solid was passed through a column packed with silica gel using benzene as the eluent. Recrystallization from petroleum ether (b.p.: 30-75°C) gave 21.2 g. (46%) of the pure product; m.p.: 64.5-65.5°C.
The NMR spectrum (CCl₄) of the compound gave absorp-
tions at δ7.35-6.60 (multiplet, 5H, aromatic H & PhCH=), 6.46
(quartet, 1H, OCH=, J_αβcis = 6.8 Hz, J_αβtrans = 14.2 Hz),
5.55 & 5.07 (AB quartet, 2H, =CH₂, J_AB = 1.3 Hz, J_AX = 17.4
Hz, J_BX = 10.6 Hz), and 4.35-3.84 (multiplet, 6H, OC=CH₂ &
OCH₂CH₂O).

Synthesis of o-, m-, and p-Vinylphenoxyethanols

2-(o-Vinylphenoxy)ethanol. 14.4 g. (0.076 mole) of o-(2-
vinylxyethoxy)styrene, 45 ml. of acetone, and 5 ml. of 10%
hydrochloric acid were placed in a 200 ml. round bottom flask
equipped with a magnetic bar. After being stirred at ambient
temperature for 30 min., the reaction was neutralized with 20%
sodium carbonate solution. After removal of the acetone on
a rotary evaporator the aqueous mixture was extracted with 50
ml. portions of chloroform twice. The combined chloroform
solution was washed with 30 ml. of water and then dried over
anhydrous sodium sulfate. Evaporation of the solvent gave an
oily residue, which was distilled on a high vacuum line
(approx. 10⁻⁴ mmHg.) by means of short path molecular distil-
alation with heating jacket temperature reading 150°C, 9.8 g.
of a white solid were obtained; m.p.: 34-35°C. The yield
was 79%.

The infrared spectrum (neat) of the compound showed
absorption bands at 3400 (s,b), 3090 (m), 3050 (m), 2940 (s),
2890 (s), 1627 (s), 1600 (s), 1580 (m), 1486 (s), 1450 (s),
1420 (m), 1376 (m), 1315 (m), 1295 (s), 1265 (s), 1165 (m),
1135 (m), 1110 (s), 1080 (s), 1050 (s), 1000 (s), 910 (s),
and 750 (s) cm⁻¹.
The NMR spectrum (CDCl₃) of the compound showed signals at δ7.45-6.63 (multiplet, 5H, aromatic H & PhCH=), 5.65 & 5.18 (AB quartet, 2H, =CH₂, J_AB = 1.7 Hz, J_AX = 17.6 Hz, J_BX = 11.0 Hz), 4.05-3.71 (multiplet, 4H, OCH₂CH₂O), and 3.05 (singlet, 1H, OH).

The ultraviolet spectrum (1,4-dioxane) of the compound gave absorption bands at 251 nm (ε = 11,400) and 300 nm (ε = 4,080).

Anal. Calcd. for C₁₀H₁₂O₂: C, 73.15; H, 7.37. Found: C, 73.02; H, 7.42.

2-(m-Vinylphenoxy)ethanol. This monomer was prepared in a manner entirely analogous to that for the previous monomer on a 0.068 mole scale. 9.1 g. (81%) of a colorless liquid was obtained by molecular distillation on a high vacuum line (approx. 10⁻⁴ mmHg.) with heating jacket reading 170°C.

The infrared spectrum (neat) of the compound showed absorptions at 3400 (s,b), 3100 (m), 3080 (m), 3020 (m), 2940 (s), 2880 (s), 1630 (m), 1600 (s), 1580 (s), 1485 (s), 1444 (s), 1415 (m), 1410 (m), 1387 (m), 1330 (m), 1310 (m), 1290 (s), 1260 (s), 1245 (s), 1172 (s), 1160 (s), 1080 (s), 1050 (s), 990 (s), 950 (s), 905 (s), 875 (m), 855 (m), 782 (s), 735 (m), 715 (s), and 665 (s) cm⁻¹.

The NMR spectrum (CDCl₃) of the compound showed signals at δ7.82-6.38 (multiplet, 5H, aromatic H & PhCH=), 5.63 & 5.16 (AB quartet, 2H, =CH₂, J_AB = 1.3 Hz, J_AX = 17.6 Hz, J_BX = 10.6 Hz), 4.08-3.73 (multiplet, 4H, OCH₂CH₂O), and 3.02 (singlet, 1H, OH).
Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.92; H, 7.37.

2-(p-Vinylphenoxy)ethanol. Hydrolysis of 3.5 g. (0.018 mole) of p-(2-vinloyxethoxy)styrene gave a solid residue. Recrystallization from low-boiling petroleum ether yielded 2.5 g. (83%) of a white crystalline solid; m.p.: 65-66°C.

The infrared spectrum (CCl$_4$) of the compound gave absorptions at 3630 (m), 3470 (m,b), 3100 (m), 3070 (w), 3050 (m), 3010 (m), 2940 (s), 2880 (m), 1630 (m), 1610 (s), 1580 (m), 1510 (s), 1455 (m), 1410 (m), 1370 (m), 1320 (m), 1300 (m), 1290 (m), 1245 (s), 1175 (s), 1115 (m), 1075 (s), 1040 (s), 990 (m), 900 (s), and 830 (s) cm$^{-1}$.

The NMR spectrum (CDCl$_3$) of the compound showed signals at 6.725-6.31 (multiplet, 5H, aromatic H & PhCH=), 5.45 & 5.01 (AB quartet, 2H, =CH$_2$, $J_{AB} = 1.2$ Hz, $J_{AX} = 17.2$ Hz, $J_{BX} = 10.6$ Hz), 4.06-3.70 (multiplet, 4H, OCH$_2$CH$_2$OH), and 2.42 (singlet, 1H, OH).

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.14; H, 7.38.

Synthesis of 2-(o-Vinlyphenoxy)ethyl Methacrylate and Acrylate

2-(o-Vinylphenoxy)ethyl methacrylate. 4.0 g. (0.024 mole) of 2-(o-vinylphenoxy)ethanol, 3.6 g. of dry pyridine, and 200 ml. of anhydrous ethyl ether were placed in a 500 ml. three-necked round bottom flask, which had been equipped with an addition funnel, a mechanical stirrer, a gas inlet, and a condenser protected by a drying tube. A slow flow of
nitrogen was maintained through the reaction. A solution of 5.0 g. (0.048 mole) of methacrylyl chloride in 25 ml. of anhydrous ether was added dropwise with constant stirring. The reaction mixture was stirred continuously overnight.

At the end of the reaction, 50 ml. of water was added to the reaction mixture. The ethereal solution was washed with 50 ml. portions of 20% sodium carbonate solution three times and with de-ionized water twice, and then dried over anhydrous magnesium sulfate. Evaporation of the ether on a rotary evaporator gave an oily residue, which contained an impurity as indicated by spectral and TLC analyses. The residual oil was passed through a column packed with silica gel using benzene as the eluent. Distillation of the chromatograph purified product on a high vacuum line gave 1.6 g. (29%) of a colorless liquid with a heating jacket temperature reading 180°C.

The infrared spectrum (neat) of the compound gave absorption bands at 3080 (m), 3040 (m), 3030 (m), 2990 (s), 2970 (s), 2930 (s), 2890 (m), 1785 (w), 1720 (s), 1640 (s), 1630 (s), 1600 (s), 1580 (m), 1490 (s), 1450 (s), 1410 (s), 1380 (m), 1345 (w), 1320 (s), 1295 (s), 1245 (s), 1170 (s), 1110 (s), 1050 (s), 1000 (s), 940 (s), 930 (s), 910 (s), 815 (m), and 750 (s) cm⁻¹.

The NMR spectrum (CDCl₃) of the compound showed signals at δ7.55-6.75 (multiplet, 5H, aromatic H & PhCH=), 6.15-5.13 (multiplet, 4H, =CH₆ & PhC=CH₂), 4.60-4.10 (multiplet, 4H, OCH₂CH₂O), and 2.0-1.90 (multiplet, 3H, CH₃).
The ultraviolet spectrum (THF) of the compound gave absorption maxima at 250 nm (ε = 13,900) and 300 nm (ε = 4,200).

**Anal. Calcd. for C\textsubscript{14}H\textsubscript{16}O\textsubscript{3}:** C, 72.39; H, 6.94. Found: C, 72.19; H, 7.12.

2-(o-Vinlyphenoxy)ethyl acrylate. The acrylate was prepared by the procedure described above for the methacrylate except that the chromatographic purification was not required. The reaction was carried out on a 0.023 mole scale. Distillation of the crude product on a high vacuum line gave 1.1 g. (22%) of a colorless liquid with heating jacket temperature reading 180°C.

The infrared spectrum (neat) of the compound gave absorption bands at 3080 (m), 3040 (m), 2960 (m), 2940 (m), 2835 (m), 1725 (s), 1625 (s), 1600 (s), 1580 (m), 1485 (s), 1450 (s), 1410 (s), 1320 (s), 1240 (s), 1185 (s), 1110 (s), 1060 (s), 985 (s), 940 (s), 910 (s), 845 (w), 810 (s), 750 (s) and 705 (m) cm\textsuperscript{-1}.

The NMR spectrum (CDCl\textsubscript{3}) of the compound showed signals at 67.55-6.75 (multiplet, 5H, aromatic H & PhCH=), 6.65-5.15 (multiplet, 5H, CH=CH\textsubscript{2} & =CH\textsubscript{2}), 4.62-4.11 (multiplet, 4H, OCH\textsubscript{2}CH\textsubscript{2}O).

**Anal. Calcd. for C\textsubscript{13}H\textsubscript{14}O\textsubscript{3}:** C, 71.54; H, 6.47. Found: C, 71.37; H, 6.65.

**Polymerization Studies**

**Anionic Polymerization of (2-Vinlyoxyethoxy)styrenes**

General procedures for the monomer and solvent purifi-
cation as well as the initiator preparation are described as follows.

**Monomer purification.** The previously prepared liquid monomer was dried over calcium hydride overnight and then redistilled before use; the solid, recrystallized monomer was dried in a desiccator, which contained phosphorus pentoxide, for one week. The purity of the monomer was checked by spectral and chromatographic analyses.

**Solvent purification.** Tetrahydrofuran (THF) was pre-dried over 5 Å molecular sieves and then redistilled from calcium hydride or lithium aluminum hydride. To the freshly redistilled THF in a 1000 ml. round bottom flask were added a small amount of potassium and sodium metal in a rough ratio of two to one and a catalytic amount of benzophenone. The flask was degassed on a high vacuum line ($10^{-4}$ mmHg.) until the deep blue-purple color of the benzophenone ketyl solution persisted.

**Initiator preparation.** A 100 ml. Schlenk-type vessel equipped with a magnetic bar was thoroughly evacuated and flamed on a high vacuum line. After 50 ml. of the THF had been condensed into the flask, it was released from the vacuum line by charging dry nitrogen or helium through the side-tube and sealed with a rubber septum. 1.5 g of resublimed naphthalene and 0.5 g. of sodium metal were quickly added when the vessel was temporarily opened and maintained under an inert atmosphere. The reaction mixture turned dark green gradually and
was stirred at ambient temperature for two hours. The concentration of the naphthalide in the solution was determined by titration against standard 0.100 N. hydrochloric acid using a mixture of methanol and de-ionized water as the solvent and phenolphthalein as the indicator.

Anionic polymerization of p-(2-vinylxyethoxy)styrene. A 100 ml. Schlenk-type vessel equipped with a magnetic bar was evacuated and flamed on a high vacuum line, followed by transferring into it 35 ml. of THF. The flask was released from the vacuum line by charging dry nitrogen through the side-tube, and was immediately sealed with a rubber septum. 8.0 g. (0.042 mole) of the monomer were added through the septum by using a dry syringe, and the solution was well stirred. After the solution had been cooled to -78°C in a dry ice-isopropanol bath, 2 ml. of the initiator solution (0.185 mmole/ml.) was injected into the flask in one shot, and the solution turned orange-red immediately, indicating the formation of the "living" styryl anion. The solution became very viscous within a few minutes and stirring was difficult. The solution was maintained at the low temperature for one hour. After the end of the reaction, the solution still maintained its characteristic color, and was terminated by adding 2 ml. of methanol. Precipitation of the polymer solution from a bulky amount of methanol gave a white powdery solid, which was filtered, washed, and dried in vacuo at ambient temperature overnight. The yield was
7.5 g. (94% conversion). The intrinsic viscosity of the polymer in benzene at 25°C was 0.438 d1/g., and the melting point of the polymer was 80-85°C. The polymer had a number-average molecular weight ($M_n$) in toluene of $2.45 \times 10^5$, which is equivalent to a degree of polymerization (DP) of 1290, and a molecular weight distribution ($M_w/M_n$) value of 1.16.

The NMR spectrum (CCl₄) of the polymer showed signals at δ7.15-5.85 (multiplet, 5H), 4.2-3.0 (multiplet, 6H), and 2.9-0.8 (multiplet, 3H).

The infrared spectrum (KBr) of the polymer gave absorption bands at 3120 (w), 3070 (m), 3030 (m), 2930 (s), 2870 (m), 1640 (s), 1620 (s), 1595 (s), 1585 (m), 1490 (s), 1450 (s), 1360 (m), 1320 (s), 1290 (m), 1240 (s), 1200 (s), 1110 (s), 1090 (s), 1050 (s), 1010 (m), 985 (s), 965(s), 930 (s), 810 (s), and 745 (s) cm⁻¹.

The ultraviolet spectrum (1,4-dioxane) of the polymer showed absorption maxima at 273.5 nm ($\varepsilon = 2,070$) and 279.5 nm ($\varepsilon = 1,830$).

**Anal. Calcd.** for $(C_{12}H_{14}O_2)_n$: C, 75.76; H, 7.42. **Found:** C, 75.67; H, 7.48.

**Anionic polymerization** of m-(2-vinylxyethoxy)styrene. The polymerization of the m-isomer was carried out twice by the same method as previously described for the o-isomer; only the second run is briefly described as follows (see Table 1, page 24, for the data of the first run). Charged to a Schlenk-type flask were 60 ml. of THF, 14.9 g. (0.078 mole) of the monomer, and 4 ml. of the initiator solution (0.190
mmole/ml.). The orange-red solution was maintained at -45°C for one hour and then terminated with 2 ml. of methanol. Precipitation of the polymer solution from methanol gave 14.9 g. (100% conversion) of a white soft gum; T_m: 35-40°C. The intrinsic viscosity of the polymer in benzene at 25°C was 0.619 dl/g. The polymer had a number-average molecular weight ($\bar{M}_n$) in toluene of $1.63 \times 10^5$, which is equivalent to a degree of polymerization (DP) of 860, and a molecular weight distribution ($\bar{M}_w/\bar{M}_n$) value of 1.97.

The infrared spectrum ($CCl_4$) of the polymer gave absorption bands at 3130 (w), 3050 (w), 2930 (s), 2890 (m), 1655 (m), 1640 (m), 1610 (s), 1600 (s), 1585 (s), 1485 (s), 1450 (s), 1365 (m), 1320 (s), 1260 (s), 1203 (s), 1160 (s), 1105 (m), 1080 (m), 1055 (m), 985 (s), 965 (m), 945 (m), 855 (m), and 700 (s) cm^{-1}.

The ultraviolet spectrum (1,4-dioxane) of the polymer showed absorption maxima a 273.5 nm ($\epsilon = 1,940$) and 279.5 nm ($\epsilon = 1,780$).

Anal. Calcd. for ($C_{12}H_{14}O_5)_n$: C, 75.76; H, 7.42. Found: C, 75.95; H, 7.34.

Anionic Polymerization of p-(2-vinyloxyethoxy)styrene. The polymerization was run twice by the procedure previously described; only the second run (see Table 1, page 24 for the first run) is described here. To a solution of 2.8 g. (0.015 mole) of the monomer in 30 ml. of refined THF was added 3 ml. of the initiator solution (0.130 mmole/ml.) after the reaction flask had been cooled to -45°C. After being stirred at
the low temperature for one hour, the dark red solution was terminated by adding 2 ml. of methanol. 2.6 g (92% conversion) of a white powdery solid were obtained by precipitation of the polymer solution from low-boiling petroleum ether. Unlike the polymeric o- and m-isomers, the polymer obtained from the p-isomer became partially insoluble within a few days. To 2.5 g. of the partially insoluble polymer was added 30 ml. of benzene, and the mixture was stirred at ambient temperature for 6 hours. Filtration of the mixture through a coarse sintered-glass funnel gave a clear solution. Reprecipitation of the benzene solution from petroleum ether gave 1.0 g (40% recovery) of a soluble polymer, which did not change its solubility characteristics over a long period of time. The intrinsic viscosity of the soluble portion of the polymer in benzene at 25°C was 0.155 dl/g. and the melting point of the polymer was 45-50°C. The polymer had a number-average molecular weight (\(M_n\)) in toluene of \(9.19 \times 10^4\), which is equivalent to a degree of polymerization (DP) of 480, and a molecular weight distribution (\(M_w/M_n\)) value of 1.11.

The infrared spectrum (KBr) of the polymer gave absorption bands at 3130 (w), 3040 (m), 2930 (s), 2890 (s), 1660 (m), 1640 (s), 1610 (s), 1587 (m), 1510 (s), 1450 (s), 1425 (w), 1370 (m), 1325 (s), 1302 (m), 1247 (s), 1200 (s), 1175 (s), 1105 (s), 1070 (s), 1050 (s), 1012 (m), 980 (s), 927 (m), 820 (s), and 700 (w) cm\(^{-1}\).
The NMR spectrum (CCl₄) of the polymer showed signals at 6.6-6.1 (multiplet, 5H), 4.2-3.7 (multiplet, 6H), and 2.2-0.6 (multiplet, 3H).

The ultraviolet spectrum (1,4-dioxane) of the polymer showed absorption maxima at 277.5 nm (ε = 1,610) and 285 nm (ε = 1,350).

**Anal. Calcd. for (C₁₂H₁₄O₂)ₙ:** C, 75.76; H, 7.42.

**Found:** C, 75.34; H, 7.18.

**Radical Polymerization of the o-, m-, and p-(2-Vinyl oxyethoxy)-styrenes**

**Radical polymerization of o-(2-vinyl oxyethoxy)styrene.** Charged to a polymer tube were 0.566 g. (2.98 mmole) of the monomer, 3.8 ml. of benzene, and 5.2 mg. of azobisisobutyronitrile (AIBN). The polymer tube was attached to a high vacuum line, frozen in a dry ice-isopropanol bath, and then evacuated. The solution was subjected to three cycles of freeze-thaw method, and the tube was then sealed under vacuum. The sealed tube containing the monomer, solvent, and initiator was placed in an oil bath set at 70°C, and was heated at this temperature for 24 hours. At the end of the polymerization, the tube was removed from the heating bath and opened. A minute amount of gel formed on the tube wall was observed. The polymer solution was poured into a large amount of petroleum ether (b.p. 30-75°C) to give a white precipitate, which was filtered, washed, and dried in a vacuum pistol at ambient temperature. The yield of the white powdery polymer was 0.245 g. (43.3% conversion). The intrinsic viscosity of the polymer in benzene at 30°C was 0.332 dL/g.
The infrared spectrum of the polymer was identical to that of the polymer obtained by anionic initiation of the same monomer; so were the melting point and solubility characteristics.

Radical polymerization of m-(2-vinylxyethoxy)styrene. The m-isomer was polymerized by the same procedure described above for the o-isomer. Charged to a polymer tube were 0.361 g. (1.90 mmole) of the monomer, 2.4 ml. of benzene, and 3.7 mg. of AIBN. The degassed and sealed tube was heated in a 70°C bath for 24 hours. Precipitation of the polymer solution from excess low-boiling petroleum ether gave 0.206 g. (57% conversion) of a white soft gum, which had exactly the same appearance as the one previously obtained by anionic polymerization. The intrinsic viscosity of the polymer in benzene at 30°C was 0.224 dl/g. The other physical properties and infrared spectrum of the polymer were identical to those of the anionic-initiated polymer.

Radical polymerization of p-(2-vinylxyethoxy)styrene. The p-isomer was polymerized under the same reaction conditions as those previously described for the o- and m-isomers. Charged to a polymer tube were 0.327 g (1.72 mmole) of the monomer, 2.2 ml. of benzene, and 3.4 mg. of AIBN. After being heated at 70°C for 24 hours, the polymer solution was precipitated from petroleum ether to give a white powdery solid. The yield was 0.126 g (38.5% conversion). It should be noted that this radically initiated polymer did not show any change in solubility over a long period of time. The
intrinsic viscosity of the polymer in benzene at 30°C was 0.222 dl/g. The other physical properties and infrared spectrum of the polymer were identical to those of the anionically initiated polymer.

**Post-Cationic Polymerization of Poly-(2-vinylxethoxy)-styrnes**

The polymer samples were dried under vacuum before use. Toluene was selected as the solvent, which was dried over calcium hydride and distilled before use.

**Post-cationic polymerization of poly[o-(2-vinylxethoxy)-styrene].** A 100 ml. Schlenk-type vessel was evacuated and flamed on a vacuum line. After cooling, 0.57 g. of the polymer and 50 ml. of toluene were added, and the vessel was flushed with dry nitrogen and capped with a rubber septum. The solution was cooled in a dry ice-isopropanol bath, and then 3 ml. of boron trifluoride gas was added by syringe. The reaction mixture was maintained at the low temperature for 2 hours. At the end of the period, the reaction contents were poured into an excess amount of methanol, centrifuged, washed, and dried in vacuum. The yield of a yellow powdery solid was 0.50 g. (88% conversion). The polymer decomposed slightly at about 300°C, and it was insoluble in all solvents tried.

The infrared spectrum (KBr and nujol) of the polymer showed absorption bands at 3070 (m), 3035 (m), 2930 (s), 2880 (s), 1600 (m), 1587(m), 1485 (s), 1445 (s), 1360 (m), 1290 (m), 1230 (s), 1115 (s), 1050 (s), 920 (m), 785 (w), and 740 (s) cm⁻¹.
Post-cationic polymerization of poly[m-(2-vinyloxyethoxy)-styrene]. Charged to a 100 ml. Schlenk-type vessel were 0.48 g. of the polymer and 50 ml. of toluene. After being cooled to -78°C, 2.5 ml. of boron trifluoride gas was introduced into the solution via a syringe, and the solution was maintained at that temperature for 2 hours. Precipitation from methanol gave 0.45 g (94% conversion) of a yellow powdery solid. The polymer was insoluble in all solvents tested, and it was slightly discolored at 300°C.

The infrared spectrum (KBr and nujol) of the polymer gave absorption bands at 3060 (m), 3030 (m), 2920 (s), 2880 (s), 1600 (s), 1585 (s), 1480 (s), 1440 (s), 1350 (m), 1256 (s), 1100 (s), 1060 (s), 950 (m), 860 (m), 777 (s), and 697 (s) cm⁻¹.

Post-cationic polymerization of poly[p-(2-vinyloxyethoxy)-styrene]. Charged to a 100 ml. Schlenk-type vessel were 0.11 g. of the polymer and 10 ml. of toluene. 0.8 ml. of boron trifluoride gas was injected into the bottle after the solution had been cooled to -78°C. The reaction was continued for 2 hours at the low temperature. Precipitation by methanol addition gave 0.091 g. (83% conversion) of a yellow solid, which slightly decomposed at 300°C. The product was insoluble in all solvents tried.

The infrared spectrum (KBr and nujol) of the polymer showed absorptions at 3030 (w), 2920 (s), 2880 (s), 1610 (s), 1580 (m), 1500 (s), 1450 (s), 1370 (m), 1295 (m), 1240 (s), 1185 (m), 1110 (m), 1070 (s), 1040 (s), 900 (s), and 820 (s) cm⁻¹.
Polyvinylphenoxyethanols from Hydrolysis of Poly-(2-vinyl oxyethoxy)styrene

Poly[2-(o-vinylphenoxy)ethanol] from hydrolysis of poly-[o-(2-vinyloxyethoxy)styrene]. 1.91 g. of the polymer, 45 ml. of acetone, and 5 ml. of 10% hydrochloric acid were mixed and stirred in a 100 ml. round bottom flask. After being stirred at ambient temperature for 24 hours, the clear polymer solution was neutralized with 1 N. methanolic ammonia. The neutralized solution was poured into 500 ml. of stirring de-ionized water, filtered, washed, and dried in vacuum at 60°C. The product was a white powdery solid and the yield was 1.59 g. (97% conversion). The polymer had an intrinsic viscosity of 0.485 d1/g. in dimethylformamide (DMF) or 0.267 d1/g. in tetrahydrofuran (THF). The melting point of the polymer was around 170-180°C.

The infrared spectrum (KBr) of the polymer gave absorption bands at 3570 (s), 3410 (b, s), 3060 (w), 3030 (w), 2930 (s), 2870 (s), 1597 (m), 1583 (m), 1490 (s), 1448 (s), 1370 (w), 1290 (m), 1240 (s), 1160 (w), 1105 (s), 1075 (s), 1034 (s), 915 (m), 890 (m), 800 (w), and 745 (s) cm⁻¹.

The NMR spectrum (CDCl₃) of the polymer showed signals at 87.3-6.2 (multiplet, 4H), 4.1-3.0 (multiplet, 4H), and 3.0-0.8 (multiplet, 4H).

The ultraviolet spectrum (1,4-dioxane) of the polymer showed absorption maxima at 274 nm (ε = 1,930) and 280 nm (ε = 1,700).

Poly[2-(m-vinylphenoxy)ethanol] from hydrolysis of poly[m-(2-vinylloxyethoxy)styrene]. 1.82 g. of the polymer was hydrolyzed by the same method as previously described for the polymeric o-isomer. Precipitation of the neutralized polymer solution from de-ionized water gave 1.51 g (96% conversion) of a white powdery solid. The melting point of the polymer was around 100-110°C and the intrinsic viscosity of the polymer in DMF was 1.27 dl/g.

The infrared spectrum (KBr) of the polymer gave absorption bands at 3360 (b, s), 3030 (w), 2920 (s), 2870 (s), 1600 (s), 1580 (s), 1480 (s), 1440 (s), 1370 (w), 1312 (m), 1250 (s), 1153 (s), 1070 (s), 1040 (s), 995 (w), 950 (m), 890 (m), 774 (s), and 693 (s) cm⁻¹.

The ultraviolet spectrum (1,4-dioxane) of the polymer gave absorption maxima at 273 nm (ε = 1,980) and 279.5 nm (ε = 1,830).

Anal. Calcd. for (C₁₀H₁₀O₂)ₙ: C, 73.14; H, 7.37. Found: C, 72.50; H, 7.23.

Poly[2-(p-vinylphenoxy)ethanol] from hydrolysis of poly[p-(2-vinylloxyethoxy)styrene]. The hydrolysis of the polymer was carried out by the same method as previously described for the polymeric o- and m-isomers except on a much smaller scale. 0.189 g. of the polymer was hydrolyzed to give 0.152 g. (93% conversion) of a white solid. The polymer product had an intrinsic viscosity in DMF of 0.219 dl/g, and a melting point of 155-165°C.
The infrared spectrum (KBr) of the polymer showed absorptions at 3390 (b, s), 3040 (w), 2930 (s), 2880 (m), 1610 (s), 1585 (m), 1510 (s), 1454 (m), 1425 (w), 1373 (ra), 1304 (m), 1245 (s), 1179 (s), 1110 (w), 1080 (s), 1050 (s), 915 (s), and 827 (s) cm\(^{-1}\).

Anal. Calcd. for \((C_{10}H_{12}O_2)_n\): C, 73.14; H, 7.37. Found: C, 71.40; H, 6.87.

Radical Polymerization of o-, m-, and p-Vinylphenoxyethanols

For these experiments, benzene and tetrahydrofuran (THF) were selected as the solvents and distilled before use.

Radical polymerization of 2-(o-vinylphenoxy)ethanol. Charged to a polymer tube were 1.40 g. (8.53 mmole) of the monomer, 5.0 ml. of benzene, and 11.3 mg. of AIBN. The solution was degassed on a vacuum line, subjected to three cycles of the free-thaw method, and then sealed under vacuum. The sealed tube was placed in an oil bath set at 70\(^{\circ}\)C, and heated at this temperature for 72 hours. During the heating period, a white precipitate gradually formed, indicating the polymer was not soluble in the solvent. At the end of the polymerization the precipitate was filtered, washed with low-boiling petroleum ether, and dried in vacuum at 60\(^{\circ}\)C. Dissolution of the dried polymer in 20 ml. of THF followed by reprecipitation from 400 ml. of petroleum ether gave 1.21 g. (86% conversion) of a white powdery solid. The intrinsic viscosity of the polymer was 0.374 dl/g. in DMF or 0.196 dl/g. in THF. The melting point, solubility characteristics, and infrared
spectrum of the polymer were identical to those of the polymer obtained from the hydrolysis of poly[o-(2-vinyl oxyethoxy)styrene].

Anal. Calcd. for \((C_{10}H_{12}O_2)_n\): C, 73.14; H, 7.37.
Found: C, 72.96; H, 7.51.

Radical polymerization of 2-(m-vinylphenoxy)ethanol. Charged to a polymer tube were 1.58 g. (9.64 mmole) of the monomer, 3.0 ml. of THF, and 3.0 mg. of AIBN. After being degassed and sealed in vacuum, the tube was heated at 60°C for 24 hours. At the end of the period, the solution became very viscous and was diluted with 10 ml. of THF. Precipitation from low-boiling petroleum ether gave 0.92 g. (58% conversion) of a white powdery solid. The intrinsic viscosity of the polymer in DMF was 1.85 dl/g. The other physical properties and infrared spectrum of the polymer were identical to those of the polymer obtained from the hydrolysis of poly[m-(2-vinyl oxyethoxy)styrene].

Anal. Calcd. for \((C_{10}H_{12}O_2)_n\): C, 73.14; H, 7.37.
Found: C, 72.05, H, 7.53.

Radical polymerization of 2-(p-vinylphenoxy)ethanol. Charged to a polymer tube were 0.604 g. of the monomer, 3.0 ml. of THF, and 3.0 mg. of AIBN. The degassed and sealed tube was heated at 60°C for 24 hours. Precipitation from low-boiling petroleum ether gave 0.278 g. (46% conversion) of a white powdery solid. The intrinsic viscosity of the polymer in DMF was 0.287 dl/g. The other physical properties as well as the infrared spectrum of the polymer were identical to
those of the polymer previously obtained from the hydrolysis of poly[p-(2-vinyloxyethoxy)styrene].

**Anal. Calcd. for** (C\(_{10}\)H\(_{12}\)O\(_2\))\(_n\): C, 73.14; H, 7.37.

**Found:** C, 73.01; H, 7.45.

### Chemical Reactions of Polyvinylphenoxyethanols

In this experiment dimethylformamide (DMF), tetrahydrofuran (THF), and pyridine were distilled from bases and stored over molecular sieves.

**Reaction of poly[2-(o-vinylphenoxy)ethanol] with 3,5-dinitrobenzoyl chloride.** In a 50 ml. glass-stoppered flask equipped with a magnetic bar were placed 0.163 g. of the polymer ([n] = 0.485 dl/g.), 0.2 g. of pyridine, 0.5 g. of the acid chloride, and 15 ml. of DMF. The reaction mixture was stirred at ambient temperature for 24 hours. Precipitation of the clear yellow solution from 300 ml. of de-ionized water gave a pale yellow solid, which was dried in a vacuum pistol at 60°C. The yield of the product was 0.310 g. (87% conversion). The intrinsic viscosity of the polymer in DMF was 0.510 dl/g. and the melting point was around 120-125°C.

The infrared spectrum (KBr and nujol) of the polymer gave absorption bands at 3110 (s), 3030 (w), 2390 (m), 2880 (m), 1730 (s), 1630 (s), 1600 (m), 1580 (m), 1540 (s), 1490 (s), 1450 (s), 1340 (s), 1275 (s), 1240 (s), 1160 (s), 1110 (m), 1070 (s), 1030 (m), 945 (m), 920 (m), 360 (w), 750 (s), and 720 (s) cm\(^{-1}\).

**Anal. Calcd. for** (C\(_{17}\)H\(_{14}\)N\(_2\)O\(_7\))\(_n\): C, 56.93; H, 3.94; N, 7.82. **Found:** C, 56.13; H, 4.12; N, 7.20.
Reaction of poly[2-(m-vinylphenoxy)ethanol] with 3,5-dinitrobenzoyl chloride. In a 50 ml. glass-stoppered flask were placed 0.160 g. of the polymer ([n] = 1.27 d1/g.), 10 ml. of DMF, 0.2 g. of pyridine, and 0.6 g. of the acid chloride. After being stirred at ambient temperature for 26 hours, the reaction contents were poured into de-ionized water, filtered, washed, and dried in vacuum. 0.324 g. (90.5% conversion) of a pale yellow solid was obtained. The intrinsic viscosity of the polymer in DMF was 0.665 d1/g. and the melting point was 85-95°C.

The infrared spectrum (KBr and nujol) of the polymer showed absorptions at 3100 (m), 2930 (m), 1730 (s), 1627 (s), 1595 (s), 1540 (s), 1480 (m), 1445 (s), 1340 (s), 1270 (s), 1160 (s), 1070 (s), 1030 (m), 920 (m), 860 (m), 770 (m), 715 (s), and 697 (m) cm⁻¹.

Anal. Calcd. for (C₁₇H₁₄N₂O₇)ₙ: C, 56.98; H, 3.94; N, 7.82. Found: C, 56.87; H, 4.01; N, 7.66.

Reaction of poly[2-(p-vinylphenoxy)ethanol] with 3,5-dinitrobenzoyl chloride. In a 50 ml. glass-stoppered flask were placed 0.084 g. of the polymer ([n] = 0.219 d1/g.), 5 ml. of DMF, 0.1 g. of pyridine, and 0.3 g. of the acid chloride. The mixture was stirred at ambient temperature for 24 hours. Precipitation from de-ionized water gave 0.163 g. (89% conversion) of a yellow solid. The intrinsic viscosity of the polymer in DMF was 0.379 d1/g. and the melting point was around 90-100°C.
The infrared spectrum (KBr and nujol) of the polymer showed absorptions at 3100 (m), 3030 (w), 2920 (s), 2880 (m), 1728 (s), 1628 (s), 1610 (s), 1585 (m), 1545 (s), 1507 (s), 1453 (m), 1345 (s), 1280 (s), 1240 (s), 1165 (s), 1110 (m), 1070 (s), 1040 (s), 910 (m), 825 (s), and 717 (s) cm\(^{-1}\).

**Anal. Calcd. for (C\(_{17}\)H\(_{14}\)N\(_2\)O\(_7\))\(_n\):** C, 56.98; H, 3.94; N, 7.82. **Found:** C, 56.75; H, 3.99; N, 7.59.

**Cyanoethylation of poly[2-(o-vinylphenoxy)ethanol].** In a 100 ml. three-necked round bottom flask equipped with a magnetic bar and condenser protected by a drying tube were added 0.140 g. of the polymer ([\(\eta\)] = 0.485 d1/g.), 10 ml. of THF, and 0.020 g. (5 weight % based on the polymer) of sodium methoxide. To the stirring solution was added 0.70 g. of redistilled acrylonitrile and the reaction mixture was heated at 40\(^\circ\)C for 24 hours. At the end of the reaction the contents were poured into methanol, filtered, and dried in vacuum. The product was a gum-like solid and the yield was 0.337 g. (62% conversion). The intrinsic viscosity of the polymer in DMF was 0.516 d1/g. and the melting point was in the range of 60-65\(^\circ\)C.

The infrared spectrum (CHCl\(_3\)) of the polymer showed absorptions at 2930 (s), 2890 (s), 2250 (m), 1600 (m), 1585 (m), 1490 (s), 1450 (s), 1360 (m), and 1125 (s) cm\(^{-1}\).

**Anal. Calcd. for (C\(_{13}\)H\(_{15}\)NO\(_2\))\(_n\):** C, 71.88; H, 6.96; N, 6.44. **Found:** C, 70.50; H, 6.69; N, 5.86.
Reaction of poly[2-(o-vinylphenoxy)ethanol] with phenyl isocyanate. In a 50 ml. glass-stoppered flask equipped with a magnetic bar were placed 0.162 g. of the polymer ([n] = 0.485 dl/g.), 15 ml. of THF, and 0.3 g. of phenyl isocyanate. The reaction mixture was stirred at ambient temperature for 24 hours. Precipitation of the clear solution from de-ionized water gave 0.256 g (94% conversion) of a white powdery solid. The intrinsic viscosity of the polymer in DMF was 0.574 dl/g. and the melting point was 170-180°C.

The infrared spectrum (KBr and nujol) of the polymer showed absorptions at 330 (s), 3290 (s), 3200 (m), 3140 (m), 3070 (m), 2940 (w), 2860 (w), 1710 (m), 1650 (s), 1590 (s), 1550 (s), 1495 (s), 1440 (s), 1315 (s), 1295 (s), 1230 (s), 1050 (m), 1025 (m), 895 (m), 750 (s), and 690 (s) cm\(^{-1}\).

Anal. Calcd. for \((C_{17}H_{17}NO_{3})_n\): C, 72.07; H, 6.05; N, 4.94. Found: C, 73.10; H, 5.53; N, 5.58.

Reaction of poly[2-(o-vinylphenoxy)ethanol] with methylene bis(4-phenyl isocyanate). In a test tube containing a solution of 0.041 g. of the polymer in 4 ml. of THF was added 0.1 g. of the diisocyanate. The mixture became cloudy while being stirred. The mixture gelled after standing at ambient temperature overnight. The contents, with stirring, were poured into water, filtered, and dried in vacuum at 60°C. The straw-colored product did not melt up to 300°C and was insoluble in any solvents tested.
The infrared spectrum (KBr and nujol) of the polymer showed absorptions at 3300 (s), 3030 (m), 2900 (m), 2250 (s), 1780 (m), 1650 (s), 1600 (s), 1540 (s), 1400 (s), 1300 (s), 1225 (s), 1100 (m), 1040 (m), 1015 (m), 910 (m), 845 (m), 800 (m), and 750 (m) cm\(^{-1}\).

Radical and Photo-Polymerization of 2-(o-Vinylphenoxy)ethyl Methacrylate and Acrylate

In this experiment tetrahydrofuran was selected as the solvent and distilled from calcium hydride before use.

**Radical polymerization of 2-(o-vinylphenoxy)ethyl methacrylate.** Charged to a polymer tube were 0.585 g. (2.52 mmole) of the monomer, 3.4 mg. of AIBN, and 11.7 ml. of THF. The tube was degassed and sealed in vacuum. The sealed tube was heated at 60°C for 6 hours; a minute amount of gel formed on the tube wall was noticed. The clear solution was poured into low-boiling petroleum ether, and a white precipitate thus formed was filtered, washed, and dried in vacuum. The yield was 0.216 g. (37% conversion). The intrinsic viscosity of the polymer in THF was 0.226 d1/g. and the melting point was greater than 300°C.

The infrared spectrum (KBr) gave absorption bands at 3070 (w), 3040 (w), 2950 (s), 2890 (m), 1805 (w), 1725 (s), 1630 (vw), 1600 (m), 1585 (m), 1490 (s), 1450 (s), 1385 (m), 1290 (m), 1225 (s), 1165 (s), 1100 (s), 1050 (m), 1000 (w), 930 (m), and 750 (s) cm\(^{-1}\).

The NMR spectrum (CDCl\(_3\)) of the polymer showed signals at 87.8-6.0 (multiplet, 4H) and 4.7-0.2 (multiplet, 12H).
The ultraviolet spectrum (THF) of the polymer showed absorption maxima at 274 nm ($\varepsilon = 1,800$) and 279 nm ($\varepsilon = 1,650$).

Anal. Calcd. for $(C_{14}H_{16}O_3)_n$: C, 72.39; H, 6.94.

Found: C, 72.34; H, 7.17.

Radical polymerization of 2-(o-vinylphenoxy)ethyl acrylate. Charged to a polymer tube were 0.550 g. (2.52 mmole) of the monomer, 3.0 mg. of AIBN, and 11.0 ml. of THF. The degassed and sealed tube was heated at 60°C for 3.25 hours. Precipitation from petroleum ether gave 0.220 g. (40% conversion) of a white solid. The intrinsic viscosity of the polymer in THF was 0.095 d1/g. and the melting point was greater than 300°C.

The infrared spectrum (KBr) of the polymer gave absorption bands at 3070 (w), 3030 (w), 2950 (s), 2880 (m), 1730 (s), 1620 (vw), 1600 (m), 1585 (m), 1490 (s), 1380 (w), 1280 (s), 1235 (s), 1160 (s), 1120 (m), 1050 (s), 925 (m), and 750 (s) cm$^{-1}$.

The NMR spectrum (CDCl$_3$) of the polymer showed signals at 67.8-6.0 (multiplet, 4H) and 5.2-0.4 (multiplet, 10H).

Anal. Calcd. for $(C_{13}H_{14}O_3)_n$: C, 71.54; H, 6.47.

Found: C, 71.41; H, 6.62.

Photo-polymerization of 2-(o-vinylphenoxy)ethyl methacrylate. Charged to a polymer tube were 0.220 g. (0.95 mmole) of the monomer and 4.5 ml. of THF. The degassed and sealed tube was irradiated at ambient temperature with a high pressure
mercury lamp for 4.5 hours. Precipitation from low-boiling petroleum ether gave 0.014 g. (6.4% conversion) of a white solid. The melting point, solubility characteristics, and infrared spectrum of the polymer were practically identical to those of the radical-initiated poly[2-(o-vinylphenoxy)-ethyl methacrylate].

**Photo-polymerization of 2-(o-vinylphenoxy)ethyl acrylate.**

Charged to a polymer tube were 0.253 g. (1.16 mmole) of the monomer and 5.1 ml. of THF. The degassed and sealed tube was subjected to ultraviolet irradiation at ambient temperature for 60 hours. Precipitation of the clear polymer solution from petroleum ether gave 0.071 g. (28% conversion) of a white solid. The melting point, solubility characteristics, and infrared spectrum of the polymer were identical to those of the radical-initiated poly[2-(o-vinylphenoxy)ethyl acrylate].
BIBLIOGRAPHY


BIOGRAPHICAL SKETCH

Shaw-Chang Chu was born on July 6, 1947 in Shanghai, China. In June, 1965, he graduated from the Normal University Secondary School. He attended the Fu-Jen University, from which he graduated in June, 1969, and was awarded the degree of Bachelor of Science in Chemistry.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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December, 1974

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